The Crystal Structures of CuP₂ and AgP₂ with some Phase Analytical Data of the Cu-P and Ag-P Systems

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The crystal structure of CuP_2 has been determined and refined using single crystal methods. The space group is $P2_1/c$ with four copper atoms in one $4(e)$ position and eight phosphorus atoms in two further sets of $4(e)$ positions. The unit cell dimensions (in Å) and the monoclinic angle are $a = 5.802$; $b = 4.807$; $c = 7.525$; $\beta = 112.68°$. X-Ray powder data show that AgP_2 is isostructural with CuP_2. The unit cell dimensions (in Å) and angle for AgP_2 are $a = 6.218$; $b = 5.056$; $c = 7.804$; $\beta = 113.48°$. It is shown that the CuP_2 structure is related to that of CdP_4. X-Ray powder investigations confirm the existence of a phase, Cu_3P, which exhibits a moderate range of homogeneity.

The occurrence of a large number of copper and silver phosphides with various compositions has been reported in earlier literature. However, a thorough investigation of the Cu—P and Ag—P systems made by Haraldsen [1,2] and by Haraldsen and Biltz,[3] indicated that the only phases in these systems are Cu_3P, CuP_2, AgP_2, and AgP_3. Haraldsen employed tensimetric analysis corroborated by X-ray powder methods. He made no quantitative interpretation of the powder photographs of CuP_2 and AgP_2 but stated that the patterns were quite different, indicating that these compounds are probably not isostructural. The powder photograph of AgP_3 was stated to be quite different from that of AgP_2.[1] The powder photograph of Cu_3P was indexed on the basis of a hexagonal unit cell, the dimensions for which were in agreement with those previously reported by Steenberg [4] (following the correction of a mistake by Steenberg in the calculation of the dimension of the a-axis). The latter author also made a structure proposal for Cu_3P based on X-ray powder data.

The present investigation was undertaken principally to determine the crystal structures of CuP_2 and AgP_2. In addition, some phase-analytical data of the Cu—P and Ag—P systems were obtained using X-ray powder methods.

EXPERIMENTAL

Preparation. The starting materials for the preparations were sheet copper (Johnsson, Matthey & Co. Ltd., London, spectrographically standardised, containing iron, silver, magnesium and silicon, each at a level of about 1 part per million or less), finely divided silver ("finsilver", R. Grave AB, Stockholm, purity higher than 99.9 %) and red phosphorus (purity higher than 99 %). Before use the copper was heated in hydrogen at a pressure of 1 atm. at 400°C for 3 h. In some preliminary phase-analytical investigations copper powder (purity probably not better than 99 %) was used; the measured cell dimensions in these preparations, however, were not significantly different from those resulting from the use of sheet copper.

The phosphides were synthesized by heating appropriate mixtures of metal powder or pieces of sheet metal with red phosphorus in evacuated and sealed silica tubes at temperatures between 500°C and 1000°C for several days. In the preparations involving sheet copper the samples were given a final heat treatment, the initial products being cooled, crushed to a fine powder and pressed into pellet form for this purpose. No attack on the silica tubes was detected. As a rule the products with higher phosphorus content were obtained as black powders but, as will be described later, it was also possible to melt some of the higher phosphides to give products with a metallic lustre. Phase-analysis of the reaction products was carried out by X-ray powder methods only.

X-Ray work. Powder photographs were recorded in Guinier-type focussing cameras using $CuK\alpha$ and $CuK\alpha_1$ radiation with silicon ($a = 5.4305$ Å) as an internal calibration standard. The accuracy of the lattice parameter measurements is estimated to be ± 0.05 %.

Single crystals with uniform cross-sections not larger than 0.05 mm were chosen. Equi-inclination Weissenberg photographs were taken using zirconium-filtered MoK radiation. The multiple film technique was used with thin iron foils interleaved between successive films. The intensities were estimated visually by comparison with a calibrated intensity scale. No correction for absorption was made. Correction for Lorentz and polarisation factors, Fourier series summations, structure factor calculations, least squares refinement, and calculations of interatomic distances were carried out on the electronic digital computer FACIT EDB using programmes devised by Lundberg,[5] by Liminga and Olovsson,[6] and by Åsbrink and Brändén.[7] Atomic scattering factors were interpolated from tables given in Vol III of the International Tables for X-ray Crystallography,[8] factors correcting for the real part of the anomalous dispersion being taken from the same source.

PHASE-ANALYTICAL INVESTIGATIONS

The Cu—P system. The present investigation confirms the results obtained by Haraldsen.[1,2] The only intermediate phases in the region 0—67 at. % phosphorus are Cu_3P and CuP_2. Lattice parameter measurements of Cu_3P in two-phase Cu—Cu_3P and Cu_3P—CuP_2 alloys indicate that the unit cell volume decreases with increasing phosphorus content, in agreement with

Table 1. Unit cell dimensions for CuP_2 and AgP_2. Estimated accuracy $\pm$ 0.05 %.

Phosphide	a (Å)	b (Å)	c (Å)	$\beta°$	U (Å³)
CuP_2	5.802	4.807	7.525	112.68	193.6
AgP_2	6.218	5.056	7.804	113.48	225.0

Table 2. Powder diffraction data up to $\sin^2\Theta = 0.30$ for CuP_2. $CuK\alpha_1$ radiation, $\lambda = 1.5405$ Å.

hkl	$\sin^2\Theta_o \times 10^4$	$\sin^2\Theta_c \times 10^4$	I_o	I_c
100	208	207	w	9.8
011	380	380	st	48.2
10$\bar{2}$	—	453	—	0.6
11$\bar{1}$	464	464	w	7.0
110				1.4
002	493	492	w	9.2
11$\bar{2}$	710	710	vv st	64.8
111				144.4
012	749	749	vw	3.9
20$\bar{2}$	829	828	m	24.6
200				8.5
102	—	946	—	2.7
21$\bar{1}$	962	962	m	19.8
020	1028	1027	w	6.7
21$\bar{2}$	1085	1085	w	8.1
210				0.1
021	1150	1150	vw	3.8
11$\bar{3}$	1202	1202	st	30.6
112				1.3
12$\bar{1}$	1234	1234	w	0.6
120				9.1
013	—	1365	—	0.0
21$\bar{3}$	1454	1454	m	14.3
211				0.1
12$\bar{2}$	1479	1480	m	9.3
121				1.0
022	1519	1520	m	16.7
30$\bar{2}$a	—	1617	—	5.3
10$\bar{4}$	1684	1684	m	12.2
22$\bar{1}$	1732	1732	m	18.9
20$\bar{4}$	1813	1813	st	16.8
202				23.7
22$\bar{2}$	1854	1855	st -	29.0
220				1.1
300	1865	1863	vvw	6.7
31$\bar{2}$	1874	1874	m+	2.9
31$\bar{1}$				23.7
11$\bar{4}$	1942	1941	m	0.1
113				15.1
004		1969		3.1
12$\bar{3}$	1973	1973	m	0.9
122				20.5
21$\bar{4}$	2071	2069	vvw	1.1
212				2.5
31$\bar{3}$	2121	2120	m	9.7
310				11.1
023	2134	2135	m	16.2
22$\bar{3}$		2224		0.0
221	2226		vvw	5.1
014		2226		3.4
30$\bar{4}$	2353	2355	vw	5.6

Table 2. Continued.

hkl	$\sin^2\Theta_o \times 10^4$	$\sin^2\Theta_c \times 10^4$	I_o	I_c
031	2433	2434	w	11.4
13$\bar{1}$	} 2518	2518	m	{ 0.5
130				16.0
31$\bar{4}$	} 2614	2612	vvw	{ 1.0
311				3.3
32$\bar{2}$	} 2644	2644	vvw	{ 2.0
32$\bar{1}$				2.3
104	2674	2669	vvw	3.1
12$\bar{4}$	} —	2711	—	{ 1.9
123				0.1
13$\bar{2}$	} 2762	2764	vw	{ 5.3
131				0.5
032	—	2804	—	0.0
40$\bar{2}$	2822	2820	vvw	4.1
22$\bar{4}$	} 2839	2840	vvw	{ 3.4
222				1.4
32$\bar{3}$	} 2892	2890	vw	{ 0.6
320				6.3
11$\bar{5}$	} 2925	2925	m	{ 15.7
114				4.4
21$\bar{5}$	} —	2931	—	{ 0.2
213				3.1
024	3000	2997	vvw	3.6

[a] This line is overlapped by a line of the calibration standard.

Haraldsen's observations. Accordingly Cu_3P has a moderate range of homogeneity, but this is certainly much narrower than the 17 at. % indicated by Moser et al.[9] A more detailed investigation of the homogeneity range of Cu_3P, together with a re-investigation of the crystal structure of Cu_3P employing single-crystal methods, has been started by the author. Results will be published later in this journal.

The single crystal investigation described later in this paper showed that CuP_2 has monoclinic symmetry. Table 1 gives the unit cell dimensions and in Table 2 powder data based on the monoclinic unit cell are given. Preliminary studies of the powder photograph suggested the possibility of indexing the structure on an orthorhombic basis. This is mere coincidence, however, arising from the geometry of the unit cell, a feature which is reflected in Table 2 where the majority of the reflexions are seen to be "overlaps" arising from two sets of crystal planes in the monoclinic structure. In spite of the high resolving power of the Guinier cameras used it was not possible to detect any splitting of these reflexions up to $\Theta = 45°$.

The unit cell dimensions for CuP_2 remain unchanged whether the measurements are made on preparations containing more or less phosphorus than the stoichiometric amount; this indicates a very small homogeneity range for the compound.

Table 3. Powder diffraction data up to $\sin^2\Theta = 0.30$ for AgP₂. Cu$K\alpha$ radiation, $\lambda = 1.5418$ Å.

hkl	$\sin^2\Theta_o \times 10^4$	$\sin^2\Theta_c \times 10^4$	I_o	I_c
100	182	182	m -	86.5
01$\bar{1}$	347	348	st	222.1
10$\bar{2}$				8.7
11$\bar{1}$	413	414	w	15.7
110				0.1
002	463	463	vw	32.8
11$\bar{2}$				99.3
111	645	646	vst	329.2
012	695	695	w	10.8
20$\bar{2}$				82.0
200	729	730	m	16.6
21$\bar{1}$	846	846	m -	65.5
102	877	877	vw	24.8
020	928	928	w	30.7
21$\bar{2}$				8.1
210	961	962	w	0.6
021	1044	1044	w	9.4
11$\bar{3}$		1109		78.7
112	1109		st	1.2
12$\bar{1}$		1111		7.2
120				28.9
013	1275	1274	vvw	0.0
21$\bar{3}$				53.6
211	1309	1309	m -	1.6
12$\bar{2}$				19.4
121	1342	1342	m -	2.7
022	1393	1392	vw	33.4
30$\bar{2}$	1411	1410	vw	19.6
22$\bar{1}$	1543	1542	w	33.4
10$\bar{4}$	1571	1572	w	33.4
300		1641		22.2
31$\bar{2}$	1643	1642	m	5.3
31$\bar{1}$				66.6
20$\bar{4}$		1656		34.0
202	1657		st	44.9
22$\bar{2}$		1658		68.5
220				0.3
11$\bar{4}$		1804		0.1
113	1806		m -	37.5
12$\bar{3}$		1806		0.0
122				51.3
004	1854	1852	vw	7.9
31$\bar{3}$				19.7
310	1876	1874	vw	15.3
21$\bar{4}$		1888		0.5
212	—		—	4.5
023	1971	1970	w	29.9
22$\bar{3}$				0.1
221	2007	2006	vvw	12.7
014	—	2085	—	2.0
30$\bar{4}$	2105	2105	vw	7.4

Table 3. Continued.

hkl	$\sin^2\Theta_o \times 10^4$	$\sin^2\Theta_c \times 10^4$	I_o	I_c
031[a]	—	2205	—	25.9
13$\bar{1}$	} 2271	2271	w	{ 1.0
130				30.2
31$\bar{4}$		} 2337		{ 2.7
311	} 2337		vvw	{ 10.2
32$\bar{2}$		} 2339		{ 9.9
32$\bar{1}$				3.0
40$\bar{2}$	—	2455	—	5.1
104		2498		5.5
12$\bar{4}$		} 2500		11.3
123	} 2502		w	0.8
13$\bar{2}$		} 2503		14.5
131				4.9
032	—	2552	—	1.9
32$\bar{3}$		} 2570		3.1
320	} 2576		w	19.4
22$\bar{4}$		} 2585		10.7
222				6.9
41$\bar{2}$	—	2687	—	0.1
21$\bar{5}$		} 2699		{ 0.0
213	} 2702		vw	{ 14.6
23$\bar{1}$		2703		9.5
11$\bar{5}$	} 2732	2730	vw	{ 35.3
114				7.1
024	2780	2781	vw	8.5
302	—	2799	—	0.2
41$\bar{3}$	} 2801	2803	vw	{ 11.9
41$\bar{1}$				3.2
23$\bar{2}$	} —	2819	—	{ 0.5
230				5.4
40$\bar{4}$	} 2919	2919	vw	{ 9.3
400				8.8
13$\bar{3}$	} 2965	2966	vw	{ 9.0
132				4.2

[a] This line is overlapped by a line of the calibration standard.

A sample with the nominal composition CuP_3 gave a powder photograph which, in addition to the diffraction pattern of CuP_2, contained several reflexions not attributable to any of the phosphorus modifications.[10] No attempt was made to index the pattern.

During the attempts to prepare good single crystals some information as to the melting point of CuP_2 was obtained. Under the conditions prevailing during preparation the melting point seems to approximate 900°C. It should be stressed, however, that the phosphorus vapor pressure in the silica tubes was not determined. In one instance a sample with the composition CuP_2 heated to 900°C gave a product which had evidently melted although some phosphorus had been simultaneously evolved. In another instance a sample with the same composition was heated to 890°C without any phosphorus losses

and judging from the appearence of the sintered lump it had been very close to the melting point.

The Ag—P system. All preparations with phosphorus contents less than 66.7 at · %. clearly demonstrated the existence of a two-phase region Ag—AgP₂. No crystallographic data have previously been reported for AgP₂. Contrary to Haraldsen's[2] observations, the powder photograph of AgP₂ showed close similarities to that of CuP₂ as is shown in Table 3. In this table the powder data for AgP₂ are indexed on the basis of a monoclinic unit cell, although, as in the instance of CuP₂, an orthorhombic unit cell could equally well have been used. The reason for choosing the monoclinic cell is discussed below. The unit cell dimensions are given in Table 1. No variation in unit cell dimensions with phosphorus content has been observed; this indicates a very small homogeneity range.

An attempt to prepare the phase designated AgP₃[1,3] was unsuccessful. A sample with the nominal composition AgP₃ was prepared by heating an appropriate mixture of silver and phosphorus at 600°C for 6 days and then cooling this to room temperature over a period of 24 h. The powder photograph showed the diffraction pattern of AgP₂ together with a few reflexions, some of which might belong to one of the phosphorus modifications.[10] However, all the reflexions could not be accounted for in this way and it is possible that the sample had not attained equilibrium.

The Cu—Ag—P system. This system has been investigated in part by Moser *et al.*[9] These authors gave no details of the phosphorus rich part of the system. It was thought valuable, as part of the present investigation, to obtain some information concerning the mutual solubility of CuP₂ and AgP₂.

Three samples with the compositions $Cu_{0.67}Ag_{0.33}P_2$, $Cu_{0.50}Ag_{0.50}P_2$, and $Cu_{0.33}Ag_{0.67}P_2$ were prepared by sintering appropriate mixtures of the phosphides at 600°C for 7 days. Visual comparison of the powder photographs of these preparations and of the binary phases showed that all the reflexions relate to a single phase which corresponds to a solid solution between CuP₂ and AgP₂. The X-ray reflexions are shifted progressively towards smaller values of the Bragg angle, Θ, with increasing silver content. These observations indicate a high probability for complete mutual solid solubility between CuP₂ and AgP₂.

THE STRUCTURE DETERMINATION AND REFINEMENT OF CuP₂

Single-crystals of CuP₂ of a quality suitable for X-ray measurements proved difficult to obtain. Fragments picked from the debris of crushed CuP₂ samples invariably gave diffraction patterns with diffuse and elongated spots, from which it would seem that the material is highly sensitive to mechanical deformation. Single-crystals giving reasonably sharp diffraction spots were finally obtained from a sample with the nominal composition CuP₂.₁ which had been heat treated at 890°C. The product was only partly melted and the crystals could be picked directly without crushing.

Rotation and Weissenberg photographs showed that the symmetry of CuP₂ is monoclinic. Weissenberg photographs were taken with the monoclinic

axis as rotation axis. The layer-lines $0 \leq k \leq 5$ were recorded. No restrictions were found limiting the occurrence of (hkl) reflexions, indicating a primitive cell. Among the $(h0l)$ reflexions only those with $l = 2n$ were detected, and in Table 2 it is seen that (010) and (030) are absent which indicates a condition for $(0k0)$ reflexions of $k = 2n$. If these extinctions are systematic the only possible space group is $P2_1/c$. A cell content of 4 formula units gives a calculated density of 4.31 g cm^{-3}. The experimental value determined by Haraldsen [2] is 4.20 g cm^{-3}.

In order to determine the atomic parameters, the Patterson projection $P(xz)$ was first calculated. On the basis of the information obtained from this projection a selected part of the Patterson space $P(xyz)$ was calculated. This confirmed the space group chosen. All strong maxima could be interpreted as arising from 4 copper and 8 phosphorus atoms in three sets of $4(e)$ positions. The atomic parameters obtained were then used to calculate values of $F(h0l)$ and $F(0kl)$, which were in their turn used to calculate the electron density projections $\varrho(xz)$ and $\varrho(yz)$. A comparison between these projections and the corresponding projections obtained using observed F values showed no discrepancies.

The refinement of the atomic parameters was performed by the least squares method employing a programme [7] devised for the FACIT EDB machine. The parameters refined were the atomic coordinates, individual isotropic temperature factors and six scale factors, one for each layer line. A weighting scheme according to Cruickshank et al.[11], $\omega = 1/(a + |F_o| + c|F_o|^2)$, was used with the final values $a = 11.3$ and $c = 0.018$. After ten cycles of refinement the shifts for all the parameters were considerably less than one-tenth of their estimated standard deviations, derived from the inverse least-squares matrix. The discrepancy factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.091 for the 593 observed independent F values. The weight analysis for the last cycle of refinement is given in Table 4. The two largest F_o values were found to be much smaller (about 20 %) than the corresponding F_c values. This is shown in Table 4 where $\overline{\omega \Delta^2}$ for these reflexions attains very large values. This effect is probably due to extinction, but in view of the good agreement between F_o

Table 4. Weight analysis for the last cycle of refinement. $\Delta = |F_o - F_c|$

Sin Θ interval	$\overline{\omega \Delta^2}$	Number of reflexions	F_o interval	$\overline{\omega \Delta^2}$	Number of reflexions
0.00 — 0.35	1.08	165	0 — 11	1.03	14
0.35 — 0.44	1.19	137	11 — 22	0.91	183
0.44 — 0.51	0.75	102	22 — 33	0.93	196
0.51 — 0.56	0.79	73	33 — 44	0.98	101
0.56 — 0.60	0.77	49	44 — 56	0.83	47
0.60 — 0.64	0.82	31	56 — 67	1.44	25
0.64 — 0.67	0.56	18	67 — 78	1.59	18
0.67 — 0.71	1.86	9	78 — 89	1.49	7
0.71 — 0.73	1.07	6	89 — 100	11.82	1
0.73 — 0.76	7.20	3	100 — 111	4.90	1

Table 5. Interatomic distances in CuP₂ (Å). Distances shorter than 3.5 Å listed. $\sigma \approx$ 0.008 Å or better.

	Cu	P_I	P_{II}
Cu	2.480, 3.402 (2)	2.320, 2.397, 2.499	2.274, 3.306, 3.435
P_I	2.320, 2.397, 2.499		2.193, 2.205, 3.262, 3.451
P_{II}	2.274, 3.306, 3.435	2.193, 2.205, 3.262, 3.451	2.207, 3.365 (2)

and F_c for the remaining reflexions no special extinction correction was considered necessary.

Interatomic distances are given in Table 5.

The final structure data of CuP₂ are as follows:

Space group $P2_1/c$ (C_{2h}^5) $Z = 4$

$a = 5.802$ Å; $b = 4.807$ Å; $c = 7.525$ Å; $\beta = 112.68°$; $U = 193.6$ Å³

All atoms are in 4(*e*) positions with the parameter values:

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	$B(\text{Å}^2)$	$\sigma B(\text{Å}^2)$
Cu	0.1435	0.0003	0.4605	0.0004	0.4158	0.0002	0.52	0.02
P_I	0.2493	0.0005	0.7788	0.0007	0.6989	0.0004	0.18	0.03
P_{II}	0.4066	0.0005	0.1147	0.0007	0.5805	0.0004	0.13	0.03

Tables of observed and calculated structure factors may be obtained on request from the Institute of Chemistry, University of Uppsala, Uppsala, Sweden.

THE CRYSTAL STRUCTURE OF AgP₂

As mentioned above, CuP₂ and AgP₂ display complete mutual solid solubility, which strongly indicates that the two phases are isostructural. This is further substantiated by the powder data presented in Table 3. The AgP₂ reflexions have been indexed on the basis of a monoclinic unit cell with dimensions similar to those of CuP₂. An intensity calculation for AgP₂, based on the atomic parameter values for CuP₂, is included in the table. The agreement between observed and calculated intensities leaves no doubt that the structure proposed for AgP₂ is substantially correct.

DESCRIPTION AND DISCUSSION OF THE CuP₂ STRUCTURE

The structure is shown in projection in Figs. 1 and 2. A convenient way to describe the structure is presented below.
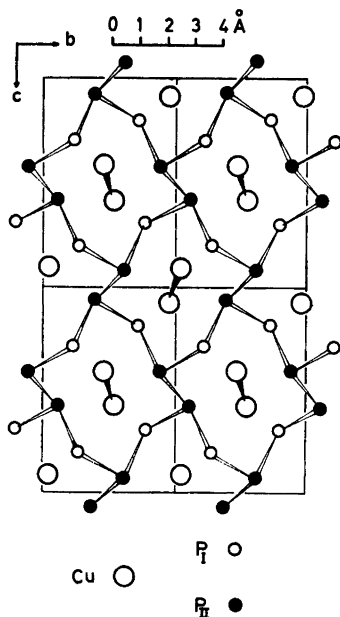
Fig. 1. The structure of CuP$_2$ projected on (100). The phosphorus network within one layer is outlined and in the middle of each phosphorus ring the copper pairs are shown.
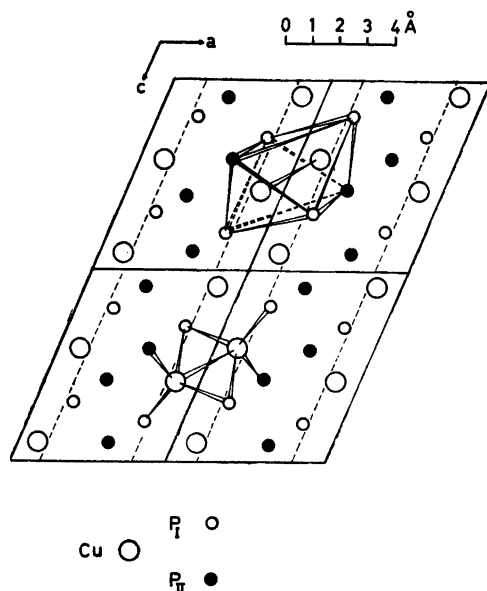
Fig. 2. The structure of CuP$_2$ projected on (010). The phosphorus layers are indicated with broken lines. In the upper part one octahedral hole between the layers is outlined and in the lower part the environment of the copper atoms is shown.

The phosphorus atoms are joined together in corrugated layers parallel with the bc-plane. Within these layers the phosphorus atoms form puckered ten-membered rings which share edges forming a two-dimensional array. In Fig. 1 the phosphorus network within such a layer is shown. As is clearly seen in Fig. 2 the phosphorus atoms actually fall into a layer arrangement, indicated in the diagram with broken lines. Thus the shortest distance between phosphorus atoms in adjacent layers is 3.60 Å, while the average value for the distances between adjacent phosphorus atoms in the rings is 2.20 Å, in agreement with the value expected from the tetrahedral covalent radius r_p = 1.10 Å. The layers are held together by copper-phosphorus bonds only. Between the layers, in the middle of the rings, there are octahedral holes in which pairs of copper atoms are situated. The distance between the copper atoms in each pair is only 2.48 Å. The distorted octahedron is outlined in Fig. 2. Each copper atom is coordinated to one copper and four phosphorus atoms, the average of the four Cu-P distances being 2.37 Å, in close agreement with the sum of the Goldschmidt C.N.12 radius for copper of 1.28 Å, and the tetrahedral covalent radius for phosphorus of 1.10 Å. The P$_I$ atom is bonded to 3 Cu atoms and 2 P atoms. The P$_{II}$ atom is coordinated tetrahedrally to 1 Cu and 3 P atoms.
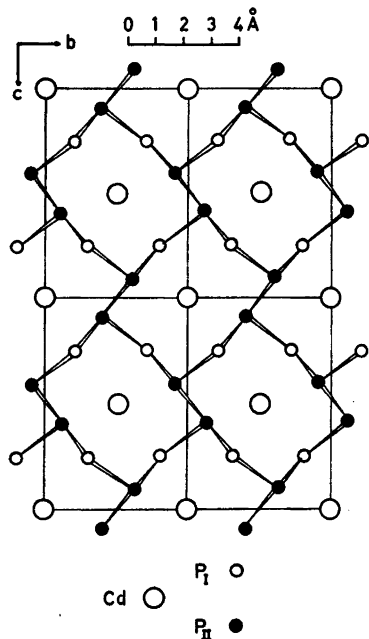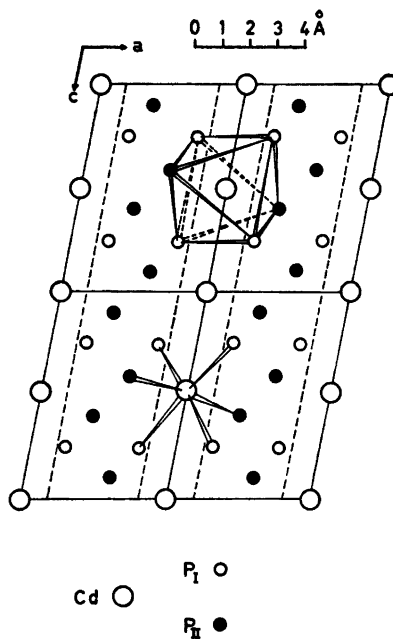
Cd ◯   P$_I$ ◯

P$_{II}$ ●

Fig. 3. The structure of CdP$_4$ projected on (100). The phosphorus network within one layer is outlined.

Fig. 4. The structure of CdP$_4$ projected on (010). The phosphorus layers are indicated with broken lines. In the upper part one octahedral hole between the layers is outlined and in the lower part the environment of the cadmium atoms is shown.

Pairs of metal atoms are also encountered in the monoclinic form of ZnP$_2$, the structure of which was recently determined by Hegyi et al.[12] Half of the zinc atoms are joined to pairs with the very short Zn—Zn distance of 2.44 Å. The phosphorus contacts do not run continuously in all three crystallographic directions but are restricted to thick layers parallel with the bc-plane. The phosphorus arrangement within the layers may be described as corresponding to spiral chains running parallel with the c-axis and connected in the [010] direction by bonds between atoms belonging to one of the four non-equivalent sets of phosphorus atoms. The zinc pairs are situated in distorted octahedral holes within the layers, while the remaining half of the zinc atoms are situated in tetrahedral holes between successive layers. As in the case of CuP$_2$ the successive phosphorus layers are thus connected by metal-phosphorus bonds only.

Another structure which provides an interesting comparison with CuP$_2$ is that of CdP$_4$, the structure of which was determined by Krebs et al.[13] The CdP$_4$ structure also belongs to the space group $P2_1/c$, two cadmium atoms occupying 2(a) positions while eight phosphorus atoms are located in two sets of 4(e) positions. Figs. 3 and 4 show the structure in projection. (In order to

facilitate the comparison with CuP_2 a unit cell with $\beta = 99.47° = 180° - 80.53°$ is used instead of the cell with $\beta = 80.53°$ originally used by Krebs *et al.*). A comparison between Figs. 1 and 2 on the one hand and Figs. 3 and 4 on the other immediately demonstrates the strong similarity between the two structures. In particular the phosphorus networks are almost identical. In accordance with the different compositions of the two compounds, in the case of CdP_4 only half the number of metal atoms require accomodation in the phosphorus lattice as compared with the number of metal atoms in CuP_2. This is achieved by placing one single cadmium atom in the octahedral holes between the phosphorus layers as opposed to a pair of copper atoms in the case of CuP_2. As is seen from Figs. 2 and 4 this leads to a somewhat less distorted octahedral coordination in CdP_4. The coordination around the phosphorus atoms in CdP_4 is distorted tetrahedral, the P_I atoms being surrounded by 2 Cd and 2 P atoms, while the P_{II} atoms are surrounded by 1 Cd and 3 P atoms. In CdP_4 the average value for the P—P distances in the rings is 2.21 Å and the average for the six shortest Cd—P distances is 2.78 Å.

Semiconductivity [14] and diamagnetism [2] have been reported for CuP_2. Both these properties can be correlated with the structural features of the compound as is shown in the following.

The relation between semiconductivity and structure has recently been discussed by Pearson [15] who considers that "a necessary condition for semiconductivity is that the anions attain filled valence subshells". If this condition is fulfilled it should "prevent arrays of chemical bonds between any atoms with vacant "metallic" orbitals in their valence shell from running continuously throughout the structure, and thus differentiate semiconductors from metals".

The condition of filled valence subshells for the anions leads Pearson to propose a general $(8-N)$ rule:

$$(n_e + b_a - b_c)/n_a = 8$$

where n_e is the total number of valence electrons, b_a is the number of valence electrons involved in anion-anion bond formation, b_c is the number of valence electrons involved in forming cation-cation bonds and n_a is the number of anions, all of these values being calculated per formula unit. Valence compounds are stated to obey this rule if they contain anions lying to the right of the Zintl border. In his article Pearson has noted that both the modifications of ZnP_2 as well as CdP_4 agree with the general $(8-N)$ rule by assuming the valence 2 for both zinc and cadmium.

Application of the general $(8-N)$ rule to CuP_2 gives $b_b = 5$, $b_c = 1$ and $n_a = 2$ which yields $n_e = 12$. The assumption that phosphorus has a valence of 5 leads to a valence of 2 for copper, which indicates that d electrons from copper are used in bond formation.

The valence 2 for copper would imply that there is an odd number of residual d electrons, a feature normally associated with paramagnetism. The copper atoms are, however, linked in pairs and it is therefore reasonable to assume that the interaction between the copper atoms results in paired electrons with antiparallel spins. This is in agreement with the diamagnetic properties reported [2] for CuP_2.

The structural comparison between CuP_2 and CdP_4 suggests that in a formal manner these two compounds can be considered as "isostructural". One cadmium atom then corresponds to one pair of copper atoms and the formula for copper diphosphide can consequently be written as Cu_2P_4. The valence of 2 obtained for copper, assuming the general $(8 - N)$ rule to be satisfied, is in agreement with this view of CuP_2. Thus one valence electron is used up in forming Cu—Cu bonds and an "effective" valence of 2 is accordingly obtained for each pair of copper atoms. This is to be compared with the valence 2 obtained for cadmium using the same rule.

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