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The Crystal Structure of Cu_3P

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In the Cu – P system, the phase commonly denoted by the formula Cu_3P has a moderate range of homogeneity, which at least at 700°C does not include the stoichiometric composition. Phase analysis by X-ray powder methods, chemical analysis and a single crystal structure analysis indicate that the homogeneity range lies approximately between $Cu_{2.82}P$ and $Cu_{2.73}P$ at 700°C.

Using single crystal diffractometry, a structure refinement has been made on a crystal of a composition corresponding to the copper-rich limit at 700°C. The ideal structure has the space group symmetry $P6_3cm$ with six formula units of Cu_3P in the unit cell. Twelve copper atoms are situated in two sets of 6(*c*) positions, four in a 4(*b*) position and two in a 2(*a*) position. The six phosphorus atoms are in a 6(*c*) position. The structure shows similarities to the previously suggested structures for Cu_3P and can be described as a complex array of interconnected PCu_6 triangular prisms with one additional copper atom outside each of the rectangular and trigonal faces of the prisms. The structure analysis indicates that the deviation from stoichiometry is associated with vacancies on the two 6(*c*) copper positions.

During an investigation of coinage metal phosphides [1,2] the crystal structure of Cu_3P has been determined using X-ray single crystal diffractometry. The Cu_3P phase has a moderate range of homogeneity which also has been the subject of some attention in the present work. Since the investigation started, Mansmann [3] has published a revision of the structure type originally proposed for Cu_3P by Steenberg.[4] Mansmann suggested that the Cu_3P structure type actually is the anti-type of LaF_3. He used six powder reflexions to differentiate between the two alternatives. Neither of the two structure proposals can, however, explain the diffraction data obtained in the present work. In the new structure type all copper atoms have both phosphorus and copper atoms as close neighbours. This was not the case in the structure type proposed by Steenberg, which has been pointed out before [5] as being unlikely. There is also a more uniform coordination in the new structure type than in the anti-LaF_3 type of structure.

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EXPERIMENTAL

Preparation. The starting materials and the procedure used to synthesise the samples have been described elsewhere.[1]

The single crystal used for collecting the intensity material was picked from an alloy with the nominal composition Cu_3P which had been melted at 1025°C and then equilibrated at 700°C for one day followed by quenching. After crushing the sample was reheated at 700°C for 3 h and quenched. Besides Cu_3P the alloy contained Cu(P) solid solution as revealed by X-ray powder photographs.

X-Ray work. Powder photographs were recorded in Guinier-type focussing cameras using $CuK\alpha$ or $CuK\alpha_1$ radiation [$\lambda(CuK\alpha) = 1.54178$ Å and $\lambda(CuK\alpha_1) = 1.54051$ Å] with silicon ($a = 5.43054$ Å) as an internal calibration standard. The errors given in this paper for the lattice parameters are standard deviations as obtained from the least squares fits.

The intensities on which the structure determination was based were measured with a manual General Electric single crystal diffractometer using rhodium filtered $AgK\alpha$ radiation and a scintillation detector with pulse height discrimination. The moving crystal-moving counter technique was used. The background was measured at each side of the scanning interval, which had three different sizes depending on the differing widths of the peaks. The stability of the X-ray generator and counter circuitry was checked by examining a standard reflexion every second hour. The intensities were corrected for Lorentz and polarisation factors but not for absorption.

Computing methods. All calculations were made on a CD 3600 computer using the programs: CELSIUS, DRF, LALS, ORFLS and DISTAN. The programs have been briefly presented elsewhere.[6,7] Atomic scattering factors and the real part of the anomalous dispersion correction were taken from tables given in Ref. 8.

STRUCTURE DETERMINATION AND REFINEMENT OF THE Cu_3P STRUCTURE

The single crystal work was started using the Weissenberg technique. The layer lines $0 \leq l \leq 9$ were recorded and carefully examined in order to determine the space group. The Laue group was found to be $6/mmm$ with $h\bar{h}0l$ reflexions occurring only when $l = 2n$ giving three possible space groups *viz.* $P6_3/mcm$, $P\bar{6}c2$ and $P6_3cm$. Both Steenberg [4] and Mansmann [3] used the space group $P\bar{3}c1$ but no reasons were found in the present investigation to use a symmetry lower than hexagonal. This conclusion is based both on the Weissenberg films and the refinement of the diffractometer data described below.

In the next stage single crystal diffractometer data were collected of a unique part of the reciprocal space with the conditions $h, k, l \leq 12$ and $2\theta \leq 75°$ and the three-dimensional Patterson function was calculated. By using the geometrical condition that interatomic vectors shorter than about 2 Å are too short to be accepted, it was possible to exclude the space groups $P6_3/mcm$ and $P\bar{6}c2$ in the interpretation of the Patterson function. A reasonable solution was found in $P6_3cm$ with eighteen copper atoms distributed on two 6(*c*), one 4(*b*) and one 2(*a*) position and with six phosphorus atoms in one 6(*c*) position. This solution was confirmed by a three-dimensional difference synthesis.

Starting with the improved positional parameters obtained from the difference synthesis, a least squares refinement was then undertaken. In addition to the positional parameters two scale factors were refined in the initial stage. (Two scale factors were used because of a breakdown of the X-ray generator during the recording of intensities leading to the necessity of using a slightly lower power during the second part of the work.) Isotropic temperature fac-

tors were then included in the refinement. These showed a tendency to become rather high for three copper positions as compared with the other positions. This is probably a combined effect of anisotropic thermal motion and vacancy formation associated with non-stoichiometry. The latter effect is discussed in the next section. In the final cycles of refinement anisotropic temperature factors were introduced. During the whole refinement procedure a weighting scheme according to Cruickshank *et al.* was used,[9] $w = (a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$, with $a = 15.0$, $c = 0.006$, and $d = 0.001$. These constants were suitable as shown by a weighting analysis. The final R-value defined as $R = \sum||F_o|-|F_c||/\sum|F_o|$ and based on the 328 reflexions used in the refinement was 0.037. For all 333 reflexions observed, $R = 0.048$.

Since there has been some controversy concerning the correct space group of Cu_3P attempts were also made to improve the result by lowering the symmetry to trigonal. The most natural way to do this is to use space group $P3c1$. However, refinement in this space group did not give any support for a lowering of the symmetry. The largest deviation for positional parameters from the refinement in $P6_3cm$ was 1.5 standard deviations. Attempts were also made to

Table 1. Structure data for copper-rich Cu_3P quenched from 700°C.

Space group: $P6_3cm$, $Z = 6$.

$a = 6.9593(5)$ Å, $c = 7.143(1)$ Å.

Atomic coordinates with standard deviations:

Atom	x	z
Cu(1) in 6(c)	0.2806(2)	0.0765(4)
Cu(2) in 6(c)	0.3761(2)	0.4246(3)
Cu(3) in 4(b)	1/3	0.1998(4)
Cu(4) in 2(a)	0	0.3213(4)
P in 6(c)	0.3322(3)	0.7500[a]

[a] Arbitrarily

Anisotropic temperature factors with standard deviations, each multiplied by 10^4. The expression used is $\exp[-(h^2\beta_{11}+hk\beta_{12}+\ldots)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	127(2)	103(2)	36(2)	103(2)	16(3)	0
Cu(2)	141(2)	300(5)	45(2)	300(5)	52(3)	0
Cu(3)	59(1)	59(1)	181(4)	59(1)	0	0
Cu(4)	57(2)	57(2)	85(3)	57(2)	0	0
P	47(2)	46(3)	24(2)	46(3)	−7(3)	0

use the structure proposal made by Mansmann [3] in space group $P\bar{3}c1$, but it proved impossible to lower the R-value below about 0.35.

The results of the structure determination and refinement are summarized in Table 1 and interatomic distances are given in Table 2. The observed and calculated structure factors are listed in Table 3.

Table 2. Interatomic distances (Å units) with standard deviations in copper-rich Cu_3P quenched from 700°C. Distances up to 4 Å are included.

Cu(1) –	P	2.360(3)	Cu(2) –	P	2.345(2)
	2 P	2.486(2)		P	2.383(2)
	Cu(2)	2.574(3)		Cu(1)	2.574(3)
	2 Cu(2)	2.595(2)		2 Cu(1)	2.595(2)
	Cu(4)	2.621(3)		Cu(1)	2.624(2)
	Cu(2)	2.624(2)		2 Cu(3)	2.713(2)
	Cu(4)	2.671(3)		Cu(4)	2.720(2)
	2 Cu(3)	2.673(2)		2 P	2.775(2)
	P	2.967(2)		2 Cu(3)	2.940(3)
	2 Cu(1)	3.382(2)		4 Cu(2)	3.787(1)
	2 Cu(3)	3.689(3)		Cu(4)	3.858(3)
				2 Cu(2)	3.966(1)
Cu(3) –	3 P	2.352(1)	Cu(4) –	3 P	2.367(2)
	3 Cu(1)	2.673(2)		3 Cu(1)	2.621(3)
	3 Cu(2)	2.713(2)		3 Cu(1)	2.671(3)
	3 Cu(2)	2.940(3)		3 Cu(2)	2.720(2)
	2 Cu(3)	3.572(0)		2 Cu(4)	3.572(0)
	3 Cu(1)	3.689(3)		3 P	3.837(3)
	3 P	3.965(3)		3 Cu(2)	3.858(3)

P –	Cu(2)	2.345(2)
	2 Cu(3)	2.352(1)
	Cu(1)	2.360(3)
	Cu(4)	2.367(2)
	Cu(2)	2.383(2)
	2 Cu(1)	2.486(2)
	2 Cu(2)	2.775(2)
	Cu(1)	2.967(2)
	Cu(4)	3.837(3)
	2 Cu(3)	3.965(3)

THE HOMOGENEITY RANGE OF Cu_3P

Information in the literature concerning the homogeneity range of Cu_3P is inconsistent.[10–12] It therefore seemed valuable to collect some further data. However, a complete determination of the phase boundaries was not attempted in the present study. A series of syntheses with nominal compositions between 24.0 and 27.5 at. % phosphorus was made by annealing each sample in evacuated silica ampoules at 700°C for one week, followed by rapid quenching in water. The lattice parameters were measured for each sample and three samples which were believed to be single phase were analysed chemically for copper

Table 3. Observed and calculated structure factors. Reflexions not included in the refinement are marked with an asterisk.

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0	0	1	87	84
0	0	2	2425	3734*
0	0	3	335	353
0	0	4	332	331
0	0	5	1177	1145
0	0	6	273	271
0	0	7	295	289
0	0	8	447	433
0	0	9	154	138
0	0	10	263	259
0	0	11	85	49*
0	0	12	213	187
1	0	0	1481	1555
1	0	1	592	611
1	0	2	229	269
1	0	3	198	199
1	0	4	186	192
1	0	5	497	483
1	0	6	225	231
1	0	7	456	453
1	0	8	193	98
1	0	9	251	74
1	0	10	52	51
1	0	11	296	295
1	0	12	327	320
1	0	13	169	186
1	0	14	248	247
1	0	15	187	198
1	1	0	208	211
1	1	1	500	561
1	1	2	135	137
1	1	3	141	144
1	1	4	269	288
1	1	5	376	378
1	1	6	156	167
1	1	7	153	174
1	1	8	396	390
1	1	9	199	207
1	1	10	331	231
1	1	11	276	284
1	1	12	123	128
1	1	13	114	110
1	1	14	596	852
1	1	15	523	513
1	1	16	568	551
1	2	0	582	544
1	2	1	204	535
1	2	2	623	201
1	2	3	299	614
1	2	4	139	298
1	2	5	232	134
1	2	6	268	240
1	2	7	257	248
1	2	8	240	159
1	2	9	182	243
1	2	10	179	118
1	2	11		185
1	2	12		179

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
1	2	13	190	178
1	2	14	185	284
1	2	15	292	232
1	2	16	230	109
1	3	0	112	220
1	3	1	226	218
1	3	2	162	168
1	3	3	118	104
1	3	4	224	126
1	3	5	117	227
1	3	6	236	240
1	3	7	187	176
1	3	8	825	838
1	3	9	561	559
1	3	10	885	188
1	3	11	117	200
1	3	12	147	146
1	3	13	415	417
1	3	14	154	150
1	3	15	147	155
1	3	16	140	138
1	3	17	108	111
1	4	0	134	129
1	4	1	340	292
1	4	2	101	113
1	4	3	278	278
1	4	4	288	267
1	4	5	149	172
1	4	6	187	192
1	4	7	122	123
1	4	8	165	134
1	4	9	122	152
1	4	10	317	129
1	4	11	146	140
1	4	12	189	176
1	4	13	126	138
1	4	14	175	184
1	4	15	161	223
1	4	16	246	173
1	4	17	188	184
1	5	0	187	184
1	5	1	120	130
1	5	2	105	100
1	5	3	150	147
1	5	4	156	123
1	5	5	125	133
1	5	6	149	132
1	5	7	599	120
1	5	8	124	463
1	5	9	209	211
1	5	10	272	268
1	5	11	297	247
1	5	12	129	138
1	5	13	132	200

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0	0	1	201	205
0	0	2	414	411
0	0	3	999	964
0	0	4	111	95
0	0	5	301	302
0	0	6	219	220
0	0	7	139	124
0	0	8	192	178
0	0	9	1447	1428
0	0	10	847	851
0	0	11	380	351
0	0	12	180	188
0	0	13	251	241
1	0	0	363	358
1	0	1	333	336
1	0	2	510	329
1	0	3	316	305
1	0	4	90	79
1	0	5	303	306
1	0	6	429	413
1	0	7	179	180
1	0	8	217	216
1	0	9	214	185
1	0	10	106	104
1	0	11	186	190
1	0	12	221	214
1	0	13	153	157
1	0	14	179	182
1	0	15	143	141
1	0	16	121	105
1	0	17	143	140
1	1	0	88	95
1	1	1	469	454
1	1	2	287	285
1	1	3	326	323
1	1	4	338	339
1	1	5	124	397
1	1	6	398	121
1	1	7	140	168
1	1	8	85	81
1	1	9	171	167
1	1	10	178	178
1	1	11	109	115
1	1	12	133	131
1	1	13	117	112
1	1	14	122	135
1	1	15	133	129
1	1	16	467	799
1	1	17	172	173
1	2	0	462	429
1	2	1	340	343
1	2	2	238	245
1	2	3	86	70
1	2	4	297	254
1	2	5	104	86
1	2	6	83	155*
1	2	7	164	180
1	2	8	81	87
1	2	9	358	354
1	2	10	173	166

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0	0	1	68	81
0	0	2	126	124
0	0	3	171	171
0	0	4	225	294*
0	0	5	998	1010
0	0	6	151	152
0	0	7	141	259
0	0	8	1222	1237
0	0	9	319	317
0	0	10	631	632
0	0	11	212	199
0	0	12	236	227
1	0	0	204	208
1	0	1	282	287
1	0	2	301	223
1	0	3	143	140
1	0	4	375	386
1	0	5	938	960
1	0	6	148	140
1	0	7	388	400
1	0	8	220	728
1	0	9	189	204
1	0	10	138	433
1	0	11	217	227
1	0	12	438	439
1	0	13	277	240
1	0	14	249	105
1	0	15	92	229
1	0	16	24	292
1	0	17	288	114
1	1	0	122	170
1	1	1	169	140
1	1	2	149	186
1	1	3	187	184
1	1	4	148	147
1	1	5	533	517
1	1	6	120	125
1	1	7	112	211
1	1	8	224	279
1	1	9	284	238
1	1	10	302	352
1	1	11	345	522*
1	1	12	71	322
1	1	13	338	159
1	1	14	160	395
1	1	15	496	278
1	1	16	219	204
1	1	17	111	110
1	2	0	230	225
1	2	1	120	129
1	2	2	138	160
1	2	3	219	223
1	2	4	241	236
1	2	5	176	178
1	2	6	160	156
1	2	7	140	139
1	2	8	148	143
1	2	9	1448	1586

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
2	1	1	227	227
2	1	2	106	97
2	1	3	154	151
2	1	4	95	96
2	2	0	199	227
2	2	1	116	292
2	2	2	1155	1178
2	2	3	552	519
2	2	4	421	434
2	2	5	684	750
2	2	6	211	214
2	2	7	113	321
2	2	8	514	508
2	2	9	242	290
2	2	10	277	337
2	2	11	1898	1908
2	2	12	825	755
2	2	13	229	233
2	2	14	208	195
2	2	15	384	396
2	2	16	762	736
2	2	17	91	91
2	3	0	909	914
2	3	1	557	557
2	3	2	333	335
2	3	3	500	553
2	3	4	357	558
2	3	5	477	469
2	3	6	208	205
2	3	7	456	444
2	3	8	629	623
2	3	9	99	108
2	3	10	215	215
2	3	11	1880	1734
2	3	12	1299	1344
2	3	13	1105	1221
2	3	14	226	227
2	3	15	153	141
2	3	16	168	163
2	3	17	144	149
2	4	0	371	380
2	4	1	91	88
2	4	2	116	113
2	4	3	1914	2115
2	4	4	1231	1262
2	4	5	162	169
2	4	6	291	289
2	4	7	201	179
2	4	8	274	282
2	4	9	886	841
2	4	10	125	125
2	4	11	177	190
2	4	12	223	225
2	4	13	267	247
2	4	14	246	234
2	4	15	209	214
2	4	16	144	141
2	4	17	148	153
2	5	0	178	178
2	5	1	164	171
2	5	2	154	153

Table 4. Unit cell dimensions and chemical analytical data for some Cu – P alloys quenched from 700°C.

Nominal composition at. %	Phases observed	Lattice parameters		Chem. analysis weight %		Calculated composition of Cu_3P
		a (Å)	*c* (Å)	Cu	P	
24.00	$Cu + Cu_3P$	6.9562(3)	7.1387(4)	–	–	–
24.50	$Cu + Cu_3P$	6.9573(4)	7.1391(6)	–	–	–
24.75	$Cu + Cu_3P$	6.9570(4)	7.1381(6)	–	–	–
25.00	Cu_3P	6.9570(5)	7.140(1)	84.81	14.42	$Cu_{2.867}P$
25.50	Cu_3P	6.9480(5)	7.133(1)	84.07	14.70	$Cu_{2.788}P$
26.00	Cu_3P	6.9352(5)	7.126(1)	83.99	14.86	$Cu_{2.755}P$
26.50	$Cu_3P + CuP_2$	6.928(1)	7.122(2)	–	–	–
27.50	$Cu_3P + CuP_2$	6.9263(5)	7.122(1)	–	–	–

and phosphorus. The results are collected in Table 4 and Fig. 1. In the calculation of the composition for the analysed alloys it has been assumed that the effect of impurities is negligible. This of course is not true but since it was found difficult to make any reliable corrections for this effect, this assumption had to be used. One sample was analysed for silicon but only 0.07 % was found and it then seems likely that the main impurity is oxygen which probably is present in oxide or phosphate phases. It may be that the impurities do not affect the relative proportions of copper and phosphorus in Cu_3P to any greater extent; however, it is not believed that the accuracy in the determination of the solubility limits of Cu_3P is very great. Despite this it seems safe to conclude that the copper rich limit of Cu_3P at 700°C is closer to 26 at. % than the stoichiometric 25 at. % and that the homogeneity range is about half an atomic percent.

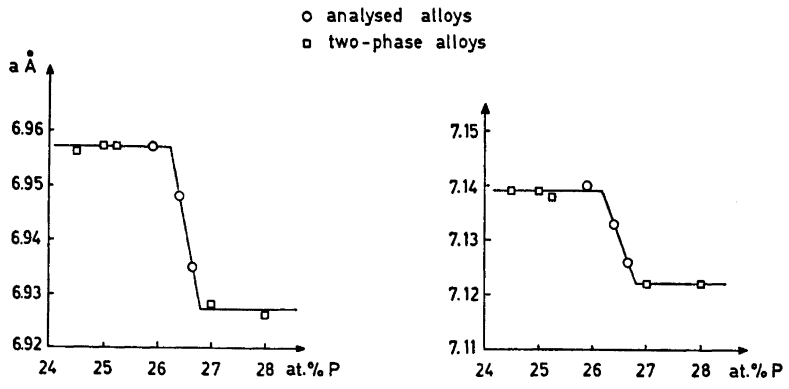

Fig. 1. Variation of the *a* and *c* axes with the composition of the Cu_3P phase. The abscissa is correct for the analysed alloys only.

Table 5. Results of refinement of the occupancy parameter for different positions in copper-rich Cu_3P quenched from 700°C.

Position	Occupancy parameter theoretical	experimental	stand. dev.
Cu(1)	0.500	0.450	0.008
Cu(2)	0.500	0.468	0.006
Cu(3)	0.333	0.325	0.005
Cu(4)	0.167	0.165	0.003
P	0.500	0.500	–

By using the single crystal diffractometer data for refining the occupancy parameters it is possible to get some information about the composition of the single crystal used. The occupancy parameter for the phosphorus position was kept constant while the others were allowed to vary. All these showed values lower than theoretical, for Cu(1) and Cu(2) with as much as 6 and 5 standard deviations, respectively; see Table 5. The positional parameters showed insignificant changes and the *R*-value was the same as before. From the result obtained the composition of the crystal is calculated to be 26.2 at. %, assuming vacancies on the Cu(1) and Cu(2) positions. Since the crystal was taken from a two-phase alloy on the copper rich side which had been annealed at 700°C the result should indicate the solubility limit on this side at that temperature. This result is in good agreement with the phase analysis and chemical analysis and supports the view that the non-stoichiometry mainly is a result of vacancies on two copper positions. If the result from the least squares refinement is interpreted as a P/Cu substitution it would correspond to a composition around 33.5 at. % phosphorus which obviously is too far from the phase analytical result. The substitution mechanism should also result in rather short P – P distances (~ 2.4 Å) which is incompatible with the crystal chemistry of metal-rich phosphides.[13]

Table 6. Unit cell dimensions for Cu_3P in two phase alloys quenched from different temperatures.

Nominal composition at. %	Quenching temperature °C	Lattice parameters *a* (Å)	*c* (Å)	Phases observed
20.0	350	6.970(1)	7.145(1)	$Cu + Cu_3P$
24.5	700	6.9573(4)	7.1391(6)	$Cu + Cu_3P$
24.5	800	6.949(1)	7.134(1)	$Cu + Cu_3P$
24.5	900	6.963(1)	7.141(1)	$Cu + Cu_3P$
30.0	400	6.940(1)	7.129(1)	$Cu_3P + CuP_2$
27.5	700	6.9263(5)	7.122(1)	$Cu_3P + CuP_2$
30.0	800	6.9265(4)	7.1219(5)	$Cu_3P + CuP_2$
30.0	850	6.9247(4)	7.1217(5)	$Cu_3P + CuP_2$

A few experiments were also performed in order to study the temperature dependence of the phase boundaries. The results are collected in Table 6. It is seen from the table and Fig. 1 that the copper-rich limit approaches the stoichiometric composition both at high and low temperature.

DESCRIPTION OF THE Cu_3P STRUCTURE

Cu_3P belongs to a new structure type. Although this structure type cannot be characterized as being a layer structure it can conveniently be described as a stacking of different types of atomic layers in the c-direction. Two different types of layers can be discerned. These are shown somewhat idealized in Fig. 2. When drawing the figure the x and y coordinates have for convenience been given as multiples of 1/3, but as is seen in Table 1 the coordinates in the actual structure deviate from this ideal value. Fig. 2a shows one of the two types of layers. It consists of copper atoms only which are in contact with

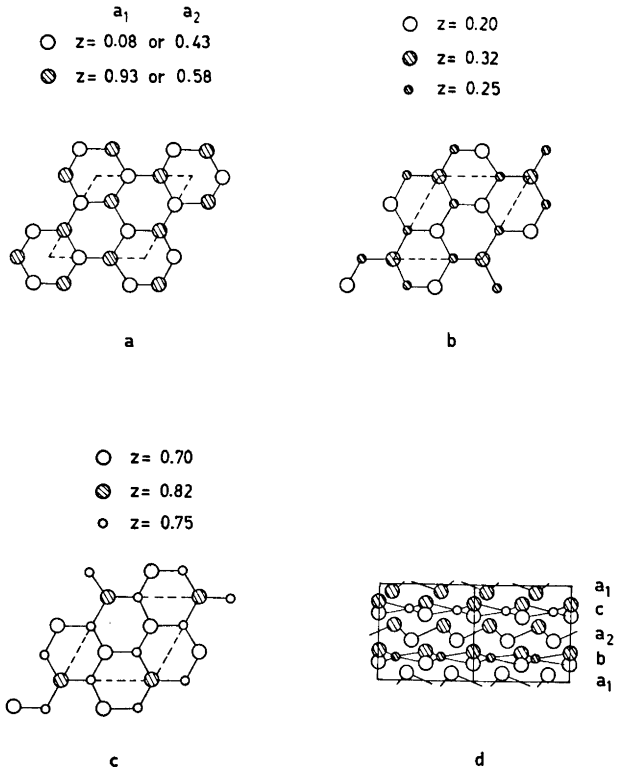

Fig. 2. The crystal structure of Cu_3P. (a) A puckered copper layer. (b) and (c) Puckered copper-phosphorus layers. (d) The stacking of the layers. Large circles represent copper atoms.

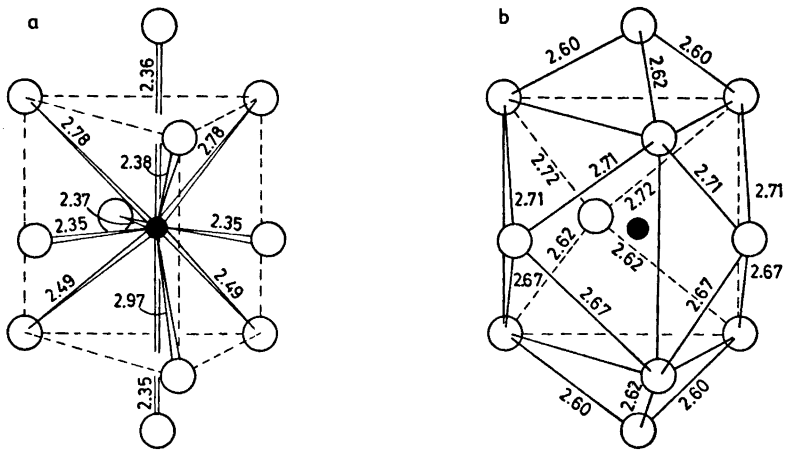

Fig. 3. The coordination polyhedron around phosphorus.

each other and form a puckered layer of six-membered rings. This type of layer exists on two different levels in each unit cell. Inserted between these layers there is the second type, which consists both of copper and phosphorus atoms. The atoms within these layers are connected in puckered six-membered rings in two different ways according to Figs. 2b and 2c. The stacking of the two types of layers is shown in Fig. 2d.

The resulting structure is characterized by rather high coordination numbers with quite large variations among the individual distances. The coordination around phosphorus can be described as triangular prismatic with one additional copper atom outside each of the three rectangular faces and the two triangular faces of the prism. In all there are eleven copper neighbours around each phosphorus atom. Of these, three neighbours are somewhat more remote than the rest. This means that the coordination polyhedron is quite irregular, a fact which is illustrated in Figs. 3a and 3b. This type of coordination based on a triangular prism around the non-metal atoms frequently occurs in transition metal phosphides as well as in borides, silicides, and carbides of transition metals. However, the coordination numbers are usually lower than eleven.

The trigonal prismatic coordination around phosphorus provides an alternative description of the Cu_3P structure. The trigonal prisms are connected to each other in layers parallel with the *ab*-plane. One such layer is illustrated in projection in Fig. 4. In each unit cell two such layers are stacked on each other in the *c*-direction in a way shown in Fig. 5. In this figure the copper atoms outside the rectangular faces of the prisms are omitted for the sake of clarity. On the other hand it is clear from the figure that each phosphorus atom has one copper neighbour outside each of the trigonal faces.

As can be seen in Table 2 the coordination around the four different types of copper atoms in Cu_3P is also quite irregular. Cu(1) has four phosphorus

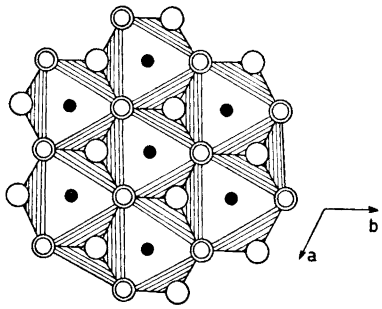

Fig. 4. A layer of trigonal prisms projected on the *ab* plane. Large circles represent copper atoms. Double circles represent two superposed atoms. Unfilled large circles are roughly at the same height as the small filled circles. The figure is somewhat idealised.

neighbours arranged in a distorted tetrahedron at distances between 2.36 Å and 2.97 Å and eight additional copper neighbours between 2.57 Å and 2.67 Å. Cu(2) too has four phosphorus atoms as neighbours in a tetrahedral arrangement at distances ranging between 2.35 Å and 2.78 Å but has in addition nine copper neighbours between 2.57 Å and 2.94 Å. Both Cu(3) and Cu(4) have three phosphorus neighbours in a trigonal pyramidal coordination and nine copper neighbours. Average values for the different types of distances are collected in Table 7 where also a comparison is made with appropriate radius sums based on the Goldschmidt radius for twelve coordination for copper, 1.28 Å, and the covalent tetrahedral radius, 1.10 Å, for phosphorus.

A comparison between the structure determined in the present work for Cu_3P and the two structures suggested earlier [3,4] shows that the largest difference is with respect to the copper atom in the two-fold position, denoted Cu(4) in this paper. In the anti-LaF_3 type of Mansmann this particular copper position has six copper neighbours and three phosphorus neighbours only, while in the structure proposed by Steenberg the coordination number is even lower with six copper atoms only. For the rest of the atoms in Cu_3P there are only minor differences between the anti-LaF_3 type and the actual structure while there are obvious differences even for these positions when the structure

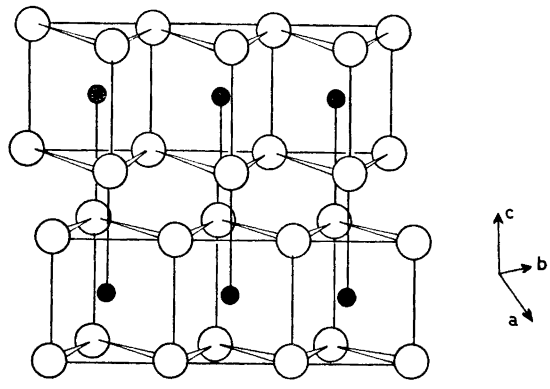

Fig. 5. The stacking of trigonal prisms in the *c* direction. Large circles represent copper atoms. Copper atoms outside the rectangular faces of the prisms are omitted.

Table 7. Environment of the different types of atoms in Cu_3P.

Atom	Number of metal neighbours	Average distance Cu – Cu	Av. dist. / $2R_{Cu}$	Number of phosphorus neighbours	Average distance Cu – P	Av. dist. / $R_{Cu}+R_P$
Cu(1)	8	2.628	1.03	4	2.575	1.08
Cu(2)	9	2.713	1.06	4	2.570	1.08
Cu(3)	9	2.775	1.09	3	2.352	0.99
Cu(4)	9	2.671	1.05	3	2.367	1.00
P	11	–	–	0	2.513	1.06

of Steenberg is considered. A considerably more uniform situation then prevails in the structure determined in the present work as far as the coordination is concerned.

It appears that the far-reaching conclusions made by Mansmann concerning the classification of a large number of compounds as belonging to the anti-LaF_3 structure type will have to be taken under reexamination. In fact, much more experimental work should be performed to settle the question of whether compounds formerly assigned to the Na_3As-family should actually belong to the Cu_3P type. In particular the possibility of phase transformations should not be overlooked, because it has recently been shown that Cu_3As undergoes a transformation at 450 – 470°C, possibly from Na_3As-type to Cu_3P-type.[14]

Note added in proof. For additional information concerning the homogeneity range and phase transformations in Cu_3P, see Ref. 15.

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