

## Synthesis and Structure of $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$ and $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$ : New Mixed Valence Compounds of the Alluaudite Structure Type.

T. E. WARNER, W. MILIUS,\* AND J. MAIER†

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Germany*

Received October 16, 1992; in revised form January 25, 1993; accepted February 1, 1993

The first example of a phase in the copper–iron–phosphorus–oxygen quaternary system ( $\text{Cu}^I, \text{Cu}^{II}$ )<sub>1.35</sub>( $\text{Fe}^{II}, \text{Fe}^{III}$ )<sub>3</sub>( $\text{PO}_4$ )<sub>3</sub>, has been prepared by a high temperature synthesis technique. The crystal structure was determined from single-crystal data and shown to be of the alluaudite type, but with differences in copper coordination and occupancy compared to the alkali and alkaline earth metal analogues. It crystallizes in the monoclinic space group  $C2/c$  with lattice constants  $a = 11.894(4) \text{ \AA}$ ,  $b = 12.629(4) \text{ \AA}$ ,  $c = 6.440(1) \text{ \AA}$ ,  $\beta = 115.24(2)^\circ$ ,  $Z = 4$ . The structure contains chains of edge sharing  $\text{FeO}_6$  octahedra linked together via the common corners of  $\text{PO}_4$  tetrahedra, yielding two distinct one-dimensional channels for copper ion occupation. The compound exhibits both copper and iron mixed valency. The copper–magnesium phosphate analogue  $\text{Cu}^I\text{Cu}^{II}\text{Mg}_3(\text{PO}_4)_3$  has been prepared and is shown to be of the same structure type,  $a = 11.85(2) \text{ \AA}$ ,  $b = 12.55(2) \text{ \AA}$ ,  $c = 6.38(1) \text{ \AA}$ ,  $\beta = 115.9(2)^\circ$ . Magnetic susceptibility measurements confirm the presence of one  $\text{Cu}^{2+}$  ( $d^9$ ) ion per unit formula with  $\mu_{\text{eff}} = 1.78 \mu_B$  ( $>50 \text{ K}$ ). © 1993 Academic Press, Inc.

### Introduction

This work is part of a continued program of exploring copper ion conductivity in solid phosphates such as  $\text{CuZr}_2\text{P}_3\text{O}_{12}$  (1), the copper analogue to the silicate free Nasicon compound (2). The fact that the sodium–iron and silver–iron analogues  $\gamma\text{-Na}_3\text{Fe}_2\text{P}_3\text{O}_{12}$  and  $\beta\text{-Ag}_3\text{Fe}_2\text{P}_3\text{O}_{12}$  were reported in the literature and shown to exhibit a very high  $\text{Na}^+$  and  $\text{Ag}^+$  ionic conductivity ( $\approx 10^{-2} \Omega^{-1}\text{cm}^{-1}$  at 600 K) (3–6), led us to explore the copper–iron–phosphorus–oxygen quaternary system. Prior to this work, no phases in this system were reported in the literature. The only three naturally occurring copper–iron phosphate minerals are hentschelite  $\text{CuFe}_2(\text{PO}_4)_2(\text{OH})_2$  (7), chalcociderite  $\text{Cu}^{II}\text{Fe}_6^{III}(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$  (8), (9)

(which is the iron-rich end member of the isomorphous series turquoise—chalcociderite  $\text{Cu}(\text{Al}, \text{Fe})_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ ), and the recently discovered mineral phosphofibrite  $\text{KCu}^{II}\text{Fe}^{III}_{15}(\text{PO}_4)_{12}(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$  (10), all of which contain hydroxide groups.

During an attempt to prepare the composition “ $\text{Cu}_3\text{Fe}_2\text{P}_3\text{O}_{12}$ ,” the first example of a copper–iron phosphate, namely the compound  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  was obtained as single crystals among the multiphase product material. The copper–magnesium phosphate analogue  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$  was also synthesized and its magnetic and structural properties discussed.

### Experimental

#### Synthesis

An attempt was made to prepare the composition “ $\text{Cu}_3\text{Fe}_2\text{P}_3\text{O}_{12}$ ” in a similar way to that for  $\text{CuZr}_2\text{P}_3\text{O}_{12}$  as described by one of us in a recent paper (1). Starting materials included copper(I)oxide (99.5%) and iron

\* Present address: Institut für Anorganische Chemie I, Universität Bayreuth, Universitätsstraße 30, 8580 Bayreuth, Germany.

† To whom correspondence should be addressed.

(II)oxide (99.999%) supplied by Johnson Matthey GmbH, and ammonium dihydrogenphosphate (99.999%) supplied by Aldrich-Chemie GmbH & Co. KG. Appropriate amounts of  $\text{Cu}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$  were weighed, then intimately ground to a fine powder with a planetary micromill (Fritsch Pulverisette) using a zirconium oxide bowl and balls for 1 hr. The calcined material was placed in an alumina boat and sintered under a flowing argon atmosphere (99.999% Ar, the balance being mainly oxygen) at a temperature of 1223 K for 10 hr before being slowly cooled to room temperature. It was clearly evident that the mixture had melted under these conditions since a severe wetting of the alumina boat had resulted in part of the material flowing out of the boat. The product was visibly inhomogeneous, with needle shaped silver-grey crystals several millimeters in length embedded in a darker colored matrix. Single crystals were selected for structural analysis, and shown below to be of the composition  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$ .

In order to prepare copper rich single phase material, a copper boat was chosen for the sintering process. This enabled the copper-iron phosphate to be prepared with a copper activity of unity. Appropriate amounts of  $\text{Cu}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$  in the molar ratio 0.675 : 1.5 : 3 were heated in a flowing argon atmosphere to 1253 K and held at this temperature for 10 hr before cooling to ambient temperature. Both heating and cooling rates were  $0.05 \text{ K sec}^{-1}$ . The reaction mixture had evidently melted, and the product was comprised of a single phase material with two crystal habits: one being silver-gray needle shaped crystals with traces of exsolved elemental copper, and the other being darker grey plate shaped crystals devoid of exsolved copper. The occurrence of exsolved elemental copper in the product indicates that a greater amount of copper is contained within the material at higher temperature in accordance with the entropic influence. Unfortunately, the product was of an insufficient crystallinity to afford single crystal structural determina-

TABLE I  
OBSERVED AND CALCULATED  $d$  VALUES, INTENSITIES, AND INDEXES

$h$	$k$	$l$	Single crystal $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$		Powder sample $\text{Cu}_{1.35+x}\text{Fe}_3(\text{PO}_4)_3$		Powder sample $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$	
			$d_{\text{cal}}/\text{\AA}$	$I_{\text{cal}}$	$d_{\text{obs}}/\text{\AA}$	$I_{\text{obs}}$	$d_{\text{obs}}/\text{\AA}$	$I_{\text{obs}}$
0	2	0	6.314	18	6.305	23		0
1	1	1	4.153	14	4.143	24	4.072	18
3	1	0	3.450	23	3.458	44	3.423	16
1	1	-2	3.078	93	3.075	53	3.090	63
2	2	-2	2.850	10	2.859	20		0
2	4	0	2.723	100	2.728	100	2.707	100
4	0	0	2.689	39	2.693	84	2.664	26
3	3	-2	2.422	11		0	2.406	13
5	1	0	2.121	10	2.126	27		0
3	1	-3	2.100	18	2.090	69	2.086	44
3	5	-2	1.922	12	1.924	20	1.911	16
2	0	-4	1.587	17		0	1.568	9
6	4	0	1.559	13		0	1.547	17

Note: Wavelength = 1.54056 Å; diffraction geometry, Guinier camera; interplanar distances are shown for  $I_{\text{cal}} \geq 10$ ; Lattice constants for  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$ ,  $a = 11.85(2) \text{ \AA}$ ,  $b = 12.55(2) \text{ \AA}$ ,  $c = 6.38(1) \text{ \AA}$ ,  $\beta = 115.9(2)^\circ$ .

tion. None the less, the powder pattern obtained on a Philips PW1710 diffractometer agrees with the peaks calculated from the single crystal data for  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  (see Table I).

The copper–magnesium phosphate analogue  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$  was prepared here for the first time. Since  $\text{Mg}^{2+}$  is a diamagnetic ion with a fixed valency, this provides an ideal opportunity to investigate the magnetic properties of the copper ions in this compound.  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$  was prepared in a copper boat under similar conditions to that for the copper–iron phosphate, using magnesium oxide (99.999%) and copper(II) oxide (99.99+) supplied by Aldrich-Chemie GmbH & Co. KG. in the molar ratio 3 : 2. The calcined powder was heated in flowing argon atmosphere to 1253 K and held at this temperature for just 1 hr before cooling to ambient temperature. The reaction mixture had evidently melted and the surface of the copper boat in contact with this melt had been etched. The product comprised essentially of dark-blue crystalline material with a slight ruby-red surface discoloration. This dark-blue material was of an insufficient crystallinity to afford single crystal structural analysis. Nevertheless, powder X-ray diffractometry showed that all the major crystallographic peaks corresponded to the alluaudite structure (see Table I). The trace amounts of surface discoloration of the product material was identified by powder XRD as  $\text{Cu}_2\text{O}$ . Chemical analysis of the bulk product material gave a copper : magnesium atomic ratio of 1.0 Cu to 0.9 Mg. This is interpreted here as corresponding to a mixture of  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$  and  $\text{Cu}_2\text{O}$ . This composition would tally at high temperatures (>1078 K) and low oxygen partial pressures ( $\approx 1$  Pa) with a mixture of  $\text{Mg}_3(\text{PO}_4)_2$  plus the copper-rich melt  $x\text{Cu}_2\text{O} \cdot \text{CuPO}_3$  as reported in reference (11). Evidence for the production of the stoichiometric compound  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$  as opposed to a material with an enriched copper solubility is presented by structural arguments together with the magnetic data given below.

### Single Crystal X-Ray Structure Determination

A silver-grey crystal with average dimensions  $0.15 \times 0.2 \times 0.2$  mm was chosen for the single crystal structure study. Intensity data was collected on a Siemens R3m/V diffractometer. Detailed crystallographic parameters are tabulated in Table II.

The crystal was shown to belong to the monoclinic system, space group  $C2/c$ . The positions of Fe and P were found by direct methods, while the positions of Cu and O were found from calculated difference Fou-

TABLE II  
CRYSTALLOGRAPHIC PARAMETERS FOR  
 $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$

Formula mass (amu)	536.59
Space group	$C2/c$
$a$ (Å)	11.894(4)
$b$ (Å)	12.629(4)
$c$ (Å)	6.440(1)
$\beta$ (degrees)	115.24(2)°
$V$ (Å <sup>3</sup> )	875.1(5)
$Z$	4
Temperature	Room temperature
$\rho$ calc. (g cm <sup>-3</sup> )	4.07
Radiation (graphite monochromated)	$\text{MoK}_\alpha$ ( $\lambda = 0.711$ Å)
Crystal size (mm)	$0.15 \times 0.2 \times 0.2$
Linear abs. coeff. (cm <sup>-1</sup> ), $\mu$	28.27
Scan type	Wyckoff scan, scan-range 1°
Scan speed (degrees/min)	min. = 1.5, max. = 19.3
No. standard reflections	3
Background to peak ratio	0.5
$2\theta$ (max)	55°
Data collected	$\pm h, k, l$
No. of unique data ( $F_0^2 > 0$ )	1099
No. of unique data with $F_0^2 > 3\sigma(F_0^2)$	935
$F_{000}$	529.92
$R/R_w$ (on $F$ for $F_0^2 > 3\sigma(F_0^2)$ )	0.0251/0.0245
No. of variables	107

TABLE III  
POSITIONAL PARAMETERS AND SITE OCCUPATION FACTORS (SOF) FOR  
 $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$

Atom	x	y	z	SOF
8f Fe(1)	0.71650(4)	0.15498(4)	0.12564(8)	1
4e Fe(2)	0	0.76164(6)	0.25	1
4e P(1)	0	0.7936(1)	0.75	1
8f P(2)	0.23648(8)	0.38823(7)	0.1287(1)	1
8f O(1)	0.6659(2)	0.8348(2)	0.8924(4)	1
8f O(2)	0.2209(2)	0.3200(2)	0.3116(4)	1
8f O(3)	0.6000(2)	0.3720(2)	0.7495(5)	1
8f O(4)	0.3757(2)	0.6040(2)	0.6863(4)	1
8f O(5)	0.1805(3)	0.5017(2)	0.6202(4)	1
8f O(6)	0.9570(2)	0.2751(2)	1.0343(4)	1
4e Cu(1)	0	0.99842(9)	0.75	0.532(4)
4b Cu(2)	0	0.5	0	0.584(4)
8f Cu(3)	0.5274(4)	0.4983(3)	0.4687(7)	0.117(2)

TABLE IV  
ANISOTROPIC THERMAL PARAMETERS FOR  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$

Atom	U11	U22	U33	U23	U13	U12
Fe(1)	0.0099(3)	0.0122(3)	0.018(3)	0.0009(2)	0.0057(2)	0.0011(2)
Fe(2)	0.0114(4)	0.0188(4)	0.0143(4)	0	0.0078(3)	0
P(1)	0.0079(5)	0.0111(6)	0.0092(5)	0	0.0030(4)	0
P(2)	0.0096(4)	0.0110(4)	0.0086(4)	-0.0002(3)	0.0044(3)	0.0002(3)
O(1)	0.091(1)	0.011(1)	0.010(1)	-0.0007(9)	0.0064(9)	-0.0002(9)
O(2)	0.012(1)	0.024(1)	0.011(1)	0.0063(9)	0.0051(9)	0.001(1)
O(3)	0.012(1)	0.012(1)	0.024(1)	0.003(1)	0.005(1)	0.001(1)
O(4)	0.013(1)	0.012(1)	0.026(1)	-0.001(1)	0.009(1)	0.0009(9)
O(5)	0.020(1)	0.014(1)	0.019(1)	0.0055(9)	0.006(1)	-0.004(1)
O(6)	0.009(1)	0.015(1)	0.008(1)	0.0005(9)	0.0023(9)	-0.0009(9)
Cu(1)	0.0089(6)	0.0075(6)	0.0392(8)	0	0.0104(5)	0
Cu(2)	0.0102(6)	0.0188(7)	0.0356(8)	-0.0058(5)	0.0079(5)	-0.0004(4)
Cu(3)	0.029(3)	0.011(2)	0.012(2)	0.001(1)	-0.0001(16)	-0.0005(18)

Note. The anisotropic thermal parameters are given in  $\text{\AA}^2$ .  $U_{ij}$  are defined for  $-2\pi^2 [h^2a^{*2} \cdot U_{11} + \dots + 2hka^*b^* \cdot U_{12}]$ .

rier synthesis. The structure was refined by full-matrix least-squares methods. The positional parameters are shown in Table III, the temperature factors are shown in Table IV, and selected bond distances and angles are listed in Table V. Further structure factor tables, all nonessential bond distances and angles, and other supporting structural detail have been deposited (12).

### Magnetic Measurements

Magnetic susceptibility measurements were obtained using a MPMS (Quantum De-

TABLE V  
IMPORTANT BOND DISTANCES (Å) AND ANGLES  
(DEGREES) FOR  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$

Fe(1)O <sub>6</sub> Octahedra	
Fe-O(3)	2.022(3)
Fe-O(5)	2.023(3)
Fe-O(1)	2.054(3)
Fe-O(2)	2.070(3)
Fe-O(6)	2.082(3)
Fe-O(2)	2.193(3)
O(3)-Fe-O(5)	91.7(1)
O(3)-Fe-O(1)	109.7(1)
O(3)-Fe-O(2)	86.4(1)
O(3)-Fe-O(6)	62.8(1)
O(3)-Fe-O(2)	81.9(1)
O(5)-Fe-O(1)	86.5(1)
O(5)-Fe-O(2)	103.1(1)
O(5)-Fe-O(6)	104.2(1)
O(5)-Fe-O(2)	170.57(9)
O(1)-Fe-O(2)	161.2(1)
O(1)-Fe-O(6)	78.4(1)
O(1)-Fe-O(2)	89.2(1)
O(2)-Fe-O(6)	83.5(1)
O(2)-Fe-O(2)	83.4(1)
O(6)-Fe-O(2)	83.1(1)
Fe(2)O <sub>6</sub> Octahedra	
Fe-O(6)	2.155(3) (2x)
Fe-O(1)	2.174(3) (2x)
Fe-O(4)	2.177(3) (2x)
O(6)-Fe-O(6)	155.0(1)
O(6)-Fe-O(1)	91.6(1) (2x)
O(6)-Fe-O(1)	74.3(1) (2x)
O(6)-Fe-O(4)	86.3(1) (2x)
O(6)-Fe-O(4)	113.6(1) (2x)
O(1)-Fe-O(1)	111.8(1)
O(1)-Fe-O(4)	161.01(9) (2x)
O(1)-Fe-O(4)	85.8(1) (2x)
O(4)-Fe-O(4)	77.8(1)

TABLE V—Continued

P(1)O <sub>4</sub> Tetrahedra	
P-O(6)	1.529(3) (2x)
P-O(3)	1.556(3) (2x)
O(6)-P-O(6)	110.7(2)
O(6)-P-O(3)	113.6(1)
O(6)-P-O(3)	108.9(2) (2x)
O(6)-P-O(3)	113.7(1)
O(3)-P-O(3)	100.9(2)
P(2)O <sub>4</sub> Tetrahedra	
P-O(5)	1.533(3)
P-O(2)	1.534(3)
P-O(1)	1.546(3)
P-O(4)	1.549(3)
O(5)-P-O(2)	110.0(2)
O(5)-P-O(1)	108.2(1)
O(5)-P-O(4)	111.3(2)
O(2)-P-O(1)	108.4(2)
O(2)-P-O(4)	108.8(2)
O(1)-P-O(4)	110.0(2)
Cu(1)O <sub>4</sub> , Cu(2)O <sub>2</sub> , Cu(3)O <sub>6</sub> Polyhedra	
Cu(1)-O(4)	1.911(3) (2x)
Cu(1)-O(3)	1.996(3) (2x)
Cu(2)-O(5)	1.963(3) (2x)
O(5)-Cu(2)-O(5)	180.000(7)
O(6)-Cu(2)-O(6)	180.000(1)
Cu(3)-O(4)	2.250(6)
Cu(3)-O(3)	2.272(5)
Cu(3)-O(3)	2.282(5)
Cu(3)-O(4)	2.341(5)
Cu(3)-O(4)	2.418(5)
Cu(3)-O(3)	2.555(6)

sign Magnetometer) operating at a constant applied magnetic field of 0.3 T in the temperature range 5 to 300 K.

### Description of the Structure and Discussion

The crystal structure of  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  ideally can be built up by a close packing of  $\frac{1}{2}[\text{FeO}_{4/2}\text{O}_2]$  chains consisting of edge sharing  $\text{FeO}_6$  octahedra and running along the  $[10\bar{1}]$  direction (see Figs. 1 and 2). The

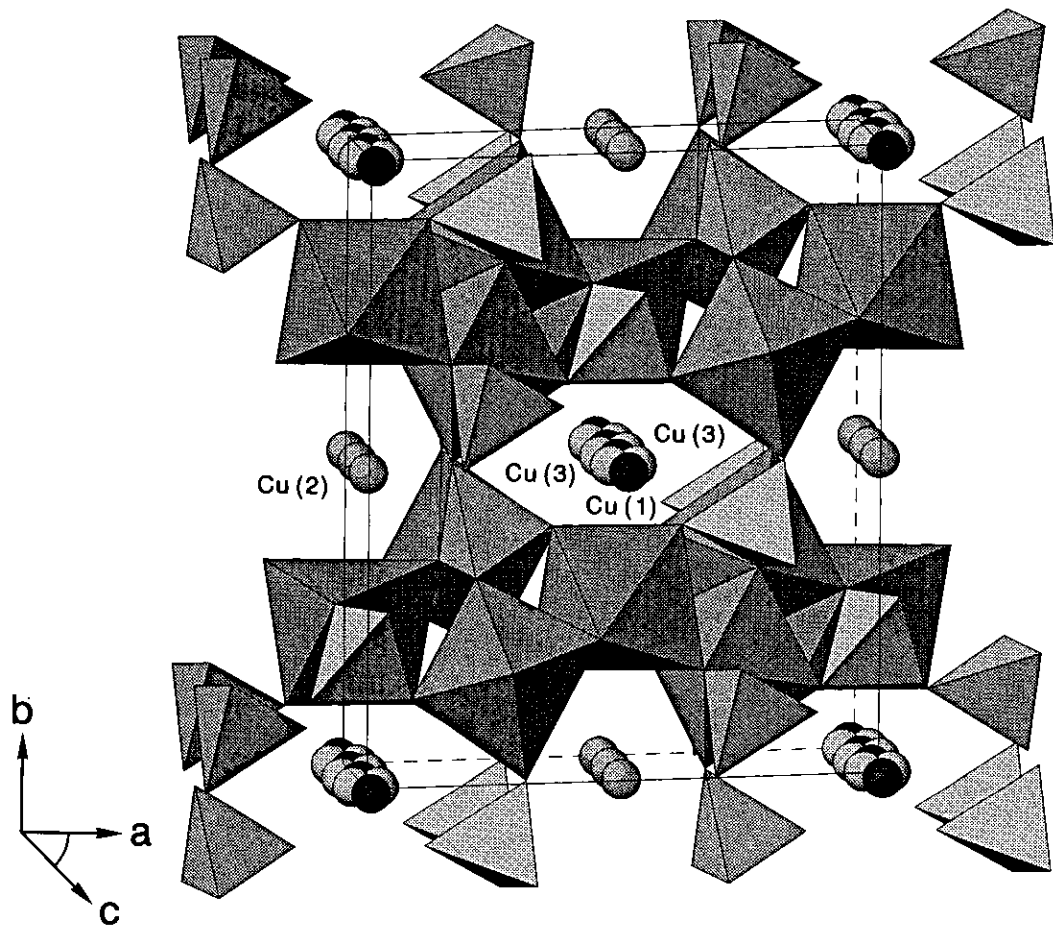


FIG. 1. Projection of the structure of  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  along the  $c$ -axis. The Cu(1) positions in channel I are shaded dark to distinguish them from the lighter shaded Cu(3) positions in this channel. The unit-cell is shown in contour.

octahedra chains are linked together via the common corners of phosphate tetrahedra. One tetrahedron always connects three chains and thus two of its oxygens belong to the same chain. In this way the three-dimensional iron phosphate substructure is constructed leading to two different kinds of channels running along the  $c$ -axis (channel I in  $(\frac{1}{2} 0 z)$ , channel II in  $(0 0 z)$ ) which contain the copper ions. All copper sites are only partially occupied.

In channel I the linearly two fold coordinated Cu(2) atoms ( $d(\text{Cu}-\text{O}) = 1.963(3) \text{ \AA}$  ( $2 \times$ ),  $\angle \text{O}-\text{Cu}-\text{O} = 180^\circ$ ) are placed (site occupation factor S.O.F. = 0.584(4)). The

distance between two copper sites along the  $c$  axis is  $\frac{1}{2}c$  ( $3.220(1) \text{ \AA}$ ). According to their coordination environment these copper ions are assumed to be  $\text{Cu}^{1+}$  (13).

The channel of type II contains the ions Cu(1) and Cu(3). Cu(1) (S.O.F. = 0.532(4)) is located in a rectangular, slightly tetrahedrally distorted environment of four oxygens ( $d(\text{Cu}(1)-\text{O})$  ranges from  $1.911(3) \text{ \AA}$  ( $2x$ ) to  $1.996(3) \text{ \AA}$  ( $2x$ )). The four oxygen atoms are part of the coordination sphere of the Cu(3) atoms: Cu(3) (S.O.F. = 0.117(2)) is coordinated by 4 oxygens at a shorter ( $2.250(6) \text{ \AA}$  to  $2.341(5) \text{ \AA}$ ) and 2 oxygens at a longer distance ( $2.418(5) \text{ \AA}$  and

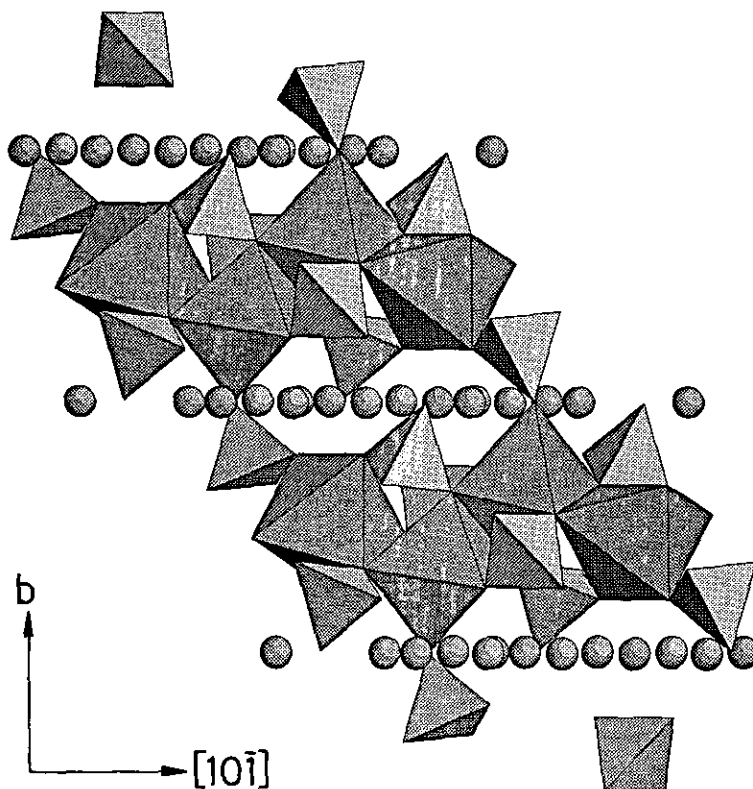


FIG. 2. Projection of the structure showing the  $\frac{1}{2}[\text{FeO}_{4/2}\text{O}_2]$  chains along  $[10\bar{1}]$ .

2.555(6) Å) forming a distorted trigonal prism. Along this channel these prisms share common rectangular faces, one face in every second prism being centered by Cu(1). The sequence of Cu(1) sites are interrupted by Cu(3) split positions leading to the period: Cu(1) (Cu(3), Cu(3)). Due to the close proximity of these copper sites together with the under-occupation and random distribution of both Cu(1) and Cu(3) ions, these copper ions may be mobile in this one-dimensional channel. Unfortunately, due to the presence of exsolved elemental copper in the product material, ionic conductivity measurements have not been possible.

The crystal structure of  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  corresponds to the alluaudite type, although the atomic coordinates of all three copper ions are shown here (see Table III) to differ from those for the alkali and alkaline earth

metal ions (X) in the classical alluaudite structure  $X(2)_4X(1)_4M(1)_4M(2)_8(\text{PO}_4)_{12}$  (14), (15).

A most interesting feature of  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  is the probable occurrence of mixed valency for both Cu and Fe. Taking  $\text{Cu}_{5.4}\text{Fe}_{12}(\text{PO}_4)_{12}$  as the unit formula, in view of the total number of possible copper sites available on spatial grounds within the unit cell (i.e. 8), there exists the possibility of a copper solid solution range between the hypothetical end members  $\text{Fe}_{12}^{\text{III}}(\text{PO}_4)_{12}$  –  $\text{Cu}_8^{\text{I,II}}\text{Fe}_{12}^{\text{II,III}}(\text{PO}_4)_{12}$ , thus containing compositions with mixed  $\text{Cu}^+/\text{Cu}^{2+}$  and mixed  $\text{Fe}^{2+}/\text{Fe}^{3+}$  valencies, (the compound  $\text{FePO}_4$  crystallizes in the berlinite structure (16)).

It is apparent that only the composition  $\text{Cu}_6^{\text{II}}\text{Fe}_{12}^{\text{II}}(\text{PO}_4)_{12}$  relates to a fixed valency for both copper and iron. All other compositions within this range must exhibit mixed valency on copper and/or iron sites. From

ionic charge and site occupation considerations for the material prepared here (i.e.  $\text{Cu}_{5.4}\text{Fe}_{12}(\text{PO}_4)_{12}$ ) the iron must be of mixed valence, while the only possibility to have a fixed copper valence is in the following two compositions:  $\text{Cu}_{5.4}^{\text{I}}\text{Fe}_{10.8}^{\text{II}}\text{Fe}_{1.2}^{\text{III}}(\text{PO}_4)_3$  and  $\text{Cu}_{5.4}^{\text{I}}\text{Fe}_{5.4}^{\text{II}}\text{Fe}_{6.6}^{\text{III}}(\text{PO}_4)_3$ .

For structural reasons concerning channel site occupation as described above together with internal redox stability regarding the coexistence of Cu(I) and Fe(III), mixed valency on the copper sites is highly probable. This is supported by the description of the copper–magnesium phosphate compound below. The occurrence of mixed valency for both iron and copper makes the experimental observation of a significant copper incorporation into the structure at high temperature more understandable.

A closer look at the Fe–O distances of the two crystallographically different Fe ions confirms the existence of two iron valence states ( $d(\text{Fe}(1)\text{--O}) = 2.074 \text{ \AA}$ ,  $d(\text{Fe}(2)\text{--O}) = 2.169 \text{ \AA}$ ,  $\angle\text{O--Fe}(1)\text{--O} 81.9^\circ$  to  $109.7^\circ$ , and  $\angle\text{O--Fe}(2)\text{--O} 74.3^\circ$  to  $113.6^\circ$ ). Classifying the Fe(1) in the  $8f$  site exclusively as  $\text{Fe}^{3+}$  and the Fe(2) in the  $4e$  site

exclusively as  $\text{Fe}^{2+}$ , the 5.4 Cu ions would require a total of 4 charge units, again leading to a highly unlikely valence state  $<1$  for Cu. For the above reasons it is not possible to fix certain crystallographic Fe sites to either valence state. Furthermore, compared to the sum of Pauling radii of  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  ( $2.05 \text{ \AA}$ ), the elongated average Fe(1)–O distance hints at the existence of mixed valence states at this Fe position. Because the copper ions in channel II also cannot clearly be fixed to a certain valence state from purely structural considerations, an absolute conclusion about the charge distribution on Cu and Fe ions in  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  cannot be drawn.

Concerning the copper–magnesium phosphate compound  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$ , the inverse magnetic susceptibility as a function of temperature is shown in Fig. 3. Above approximately 50 K the Curie–Weiss law is obeyed ( $\theta = -49.35 \text{ K}$ ,  $C = 0.3968 \text{ emu K mol}^{-1}$ ) which indicates that  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$  is paramagnetic with an effective magnetic moment  $\mu_{\text{eff}} = 1.78 \mu_{\text{B}}$ . This is very close to the value  $1.73 \mu_{\text{B}}$  for idealized free spin  $s = \frac{1}{2}$ , indicating that the compound con-

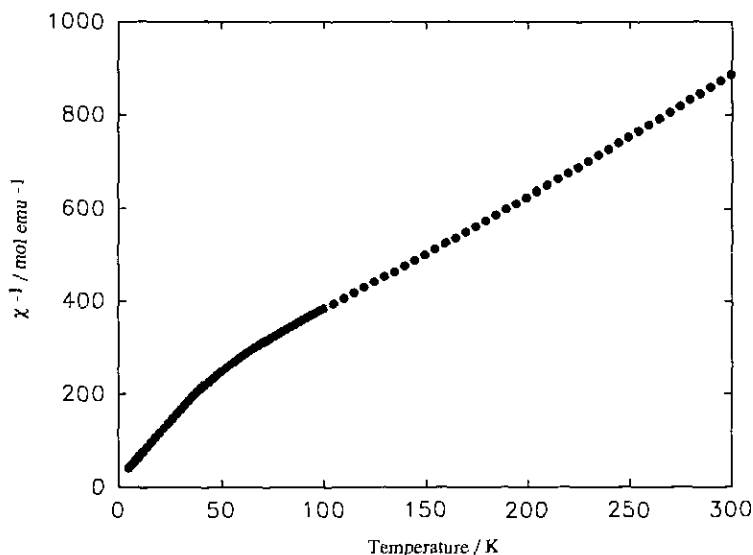


FIG. 3. Reciprocal magnetic susceptibility as a function of temperature for  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$  in an applied field of 0.3 T.



tains one  $\text{Cu}^{2+}$  per unit formula, hence  $\text{Cu}^{\text{I}}$   $\text{Cu}^{\text{II}}$   $\text{Mg}_3(\text{PO}_4)_3$ . If analogy is made with the copper-iron phosphate compound where channel I is assumed to be occupied solely by  $\text{Cu}^+$  ions, then this result suggests that at least one of the copper sites in channel II (i.e.  $\text{Cu}(1)$  or  $\text{Cu}(3)$ ) of the alluaudite structure must contain a  $\text{Cu}^{2+}$  ion. Below approximately 50 K magnetic interaction reduces the effective magnetic moment to  $\mu_{\text{eff}} = 1.27 \mu_{\text{B}}$ , indicating that at low temperatures  $\approx 50\%$  of the original moments are lost.

### Conclusions

$\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  and  $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$  have been prepared and shown to be of the alluaudite structure type. The copper ions were shown to occupy different coordination sites compared to the alkali and alkaline earth metal ions in the classical alluaudite structure. The occurrence of mixed valence for both Cu and Fe, along with an extended copper solubility in the first compound is illustrated. A detailed analysis of the valence states was not possible. In contrast to this, X-ray diffractometry and magnetic measurements for the magnesium compound conclude an equimolar copper mixed valency, hence  $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{Mg}_3(\text{PO}_4)_3$ .

With regard to  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  it is tentatively suggested that in channel II, due to the close proximity of the copper sites together with the under-occupation and random distribution of both  $\text{Cu}(1)$  and  $\text{Cu}(3)$  ions, these copper ions may be mobile in this one-dimensional channel. In the iron compound this is supported by the observation of exsolved elemental copper during cooling from high temperatures, which indicates a copper ion mobility coupled with an electronic conductivity. Electrical and conductivity studies are being performed.

### Acknowledgments

The authors are grateful to L. Viczian for the powder XRD patterns, to Dr. K. Peters for the single crystal XRD measurements, and to Dr. R. Kremer for both the magnetic susceptibility measurements and for discussions concerning this work. Discussions with Dr. W. Hönlé are also very much appreciated. We are also indebted to him for reading the manuscript. We also thank O. Buresch for the chemical analysis and B. Reichert, U. Riedel, E. Brücher, and P. Senk for technical assistance.

### References

1. T. E. WARNER, P. P. EDWARDS, AND D. J. FRAY, *Mater. Sci. Eng. B* **8**, 219 (1991).
2. K-D. KREUER, H. KOHLER AND J. MAIER, in "High Conductivity Ionic Conductors: Recent Trends and Application, (T. Takahashi, Ed.), p. 242 World Scientific, Singapore, (1989).
3. M. PINTARD-SCRÉPEL, F. D'YVOIRE, AND F. REMY, *C. R. Acad. Sci. Paris Ser C* **286**, 381 (1978).
4. J. M. WINAND, A. RULMONT, AND P. TARTE, *J. Mater. Sci.* **25**, 4008 (1990).
5. F. D'YVOIRE, M. PINTARD-SCRÉPEL, E. BRETEY, AND M. DE LA ROCHÈRE, *Solid State Ionics* **9 & 10**, 851 (1983).
6. J. C. COUTURIER, J. ANGENAULT, AND M. QUARTON, *Mater. Res. Bull.* **26**, 1009 (1991).
7. N. H. W. SIEBER, E. TILLMANN, AND W. HOFMEISTER, *Acta Crystallogr. Sect. C* **43**, 1855 (1987).
8. H. CID-DRESDUER, *Am. Mineral.* **50**, 227 (1965).
9. G. GIUSEPPETTI, F. MAZZI AND C. TADINI, *N. Jb. Miner. Mh. H* **5**, 227 (1989).
10. K. WALENTA, AND P. J. DUNN, *Chem. Erde* **43**, 11 (1984).
11. M. C. BALL, *J. Chem. Soc. A* 1113 (1968).
12. Additional crystal data has been deposited at the Fachinformationszentrum Karlsruhe, D-7514 Eggstein-Leopoldshafen 2, Germany. Inquiries should be accompanied by the depository number CSD 55964, the names of the authors, and the literature citation.
13. H. K. MÜLLER-BUSCHBAUM, *Angew. Chem.* **103**, 741 (1991).
14. P. B. MOORE, *Am. Mineral.* **56**, 1955 (1971).
15. O. V. YAKUBOVITCH, M. A. SIMONOV, YU. K. EGOROV-TISMENKO AND N. V. BELOV, *Dokl. Akad. Nauk SSSR* **236**, 1123 (1977). [English translation *Sov. Phys. Dokl.* **22** (10), 550 (1977)]
16. H. N. NG AND C. CALVO, *Can. J. Chem.* **53**, 2064 (1975).