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The antiferromagnetic structure of triclinic copper(II) phosphate

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Abstract. The antiferromagnetic structure of triclinic $\text{Cu}_3(\text{PO}_4)_2$ ($T_N = 22.2(5)$ K) has been determined at 2 K by unpolarised neutron diffraction from powdered and single-crystal samples prepared by hydrothermal synthesis. The triacut reduced chemical unit cell has $a = 4.855(1)$, $b = 5.288(1)$, $c = 6.184(1)$ Å, $\alpha = 72.34(1)$, $\beta = 86.99(1)$ and $\gamma = 68.54(1)^\circ$ at ambient temperature and $a = 4.848(1)$, $b = 5.280(1)$, $c = 6.183(1)$ Å, $\alpha = 72.30(1)$, $\beta = 86.90(1)$ and $\gamma = 68.59(1)^\circ$ at 6 K: it contains one formula unit and its space group is $P\bar{1}$. The magnetic propagation vector is $(00\frac{1}{2})$ referred to this cell and, within the accuracy of the determination, the magnetic structure is collinear with equal moments of $0.68(1) \mu_B$ on each of the two crystallographically inequivalent Cu^{2+} ions. The Cu1 ion is at an inversion centre which is preserved in the magnetic space group $P_{2_1}\bar{1}$. The Cu1 moment points in a direction $\theta = 72(2)^\circ$, $\varphi = 135(2)^\circ$ with the Cu2 moments antiferromagnetically coupled to the Cu1 moment; here θ and φ are the polar angles referred to the orthogonal crystal axes with $[001]$ as the polar axis (z), and x along a^* . The φ -angles are measured from the x, z plane. The magnetic form factor is found to be expanded by 14(3)% relative to that calculated for free Cu^{2+} ion wave functions. The magnetic exchange paths through the structure are discussed.

1. Introduction

We are currently investigating the magnetic structures of first-group transition metal phosphates in an attempt to quantify the roles played by exchange, single-ion anisotropy and covalency in determining their magnetisation. Our recent work has included studies of cobalt orthophosphate, $\text{Co}_3(\text{PO}_4)_2$ and diphosphate, $\text{Co}_2\text{P}_2\text{O}_7$ (Forsyth *et al* 1988b, 1989). As part of this programme, we now report the antiferromagnetic structure of $\text{Cu}_3(\text{PO}_4)_2$ which we have determined from powder and single-crystal unpolarised neutron diffraction data collected at 6 and 2 K respectively.

The crystalline powder was prepared by hydrothermal synthesis in which appropriate amounts of Cu, HNO_3 , H_3PO_4 and H_2O were heated at 500 K for two days in a Teflon lined steel container. Crystals of $\text{Cu}_3(\text{PO}_4)_2$ with dimensions normally less than one millimetre were produced. The largest of these were selected for the single-crystal neutron work and the remainder crushed to a powder with particle sizes between 300 and 450 μm . The magnetic susceptibility of the powder was measured at the Laboratoire

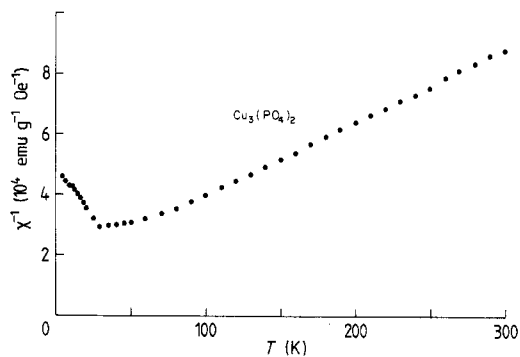


Figure 1. The variation of the inverse magnetic susceptibility of powdered $\text{Cu}_3(\text{PO}_4)_2$ as a function of temperature. A Néel point of 30(1) K is indicated.

Louis Néel, Grenoble, with the results illustrated in figure 1. The material clearly becomes antiferromagnetic, with a Néel temperature in the region of 30 K.

The crystal structure of triclinic $\text{Cu}_3(\text{PO}_4)_2$ has been determined by Shoemaker *et al* (1977). These authors also used hydrothermal synthesis to grow single crystals of a size sufficient for x-ray diffractometry and showed that the material is isostructural with the mineral stranskiite, $\text{Zn}_2\text{Cu}(\text{AsO}_4)_2$. At room temperature they report the parameters of the reduced unit cell as

$$\begin{aligned} a &= 4.8537(7) \text{ \AA} & b &= 5.2855(6) \text{ \AA} & c &= 6.1821 \text{ \AA} \\ \alpha &= 72.35(1)^\circ & \beta &= 86.99(1)^\circ & \gamma &= 68.54(1)^\circ. \end{aligned}$$

The space group is $\text{P}\bar{1}$ with $Z = 1$; the Cu^{2+} ion Cu1 occupies an inversion centre and is surrounded by two oxygen atoms at 1.924 Å and two at 1.982 Å forming a slightly distorted square-planar coordination. Cu2 lies in an irregular polyhedron of five oxygen atoms: four at an average distance of 1.965 Å and a fifth at 2.265 Å, giving an average for five-fold coordination of 2.025 Å (the next nearest oxygen is at 3.06 Å). Table 1 lists the atomic positional and thermal parameters obtained by Shoemaker *et al* (1977) and figure 2 illustrates the structure.

2. Neutron powder diffraction

The quality of our sample was checked using the high-resolution neutron time-of-flight diffractometer (HRPD) at the ISIS pulsed spallation source, Rutherford Appleton Laboratory. Data were collected at ambient temperature and at 6 K using the backward-angle detector bank. The sample was held in a slab cell with vanadium windows and in a vanadium-tailed cryostat, so the spectra were not contaminated by peaks from the sample environment. The ambient temperature data extended in d -spacing from 0.62 to 6.2 Å. The profile in the range 0.735–2.28 Å was refined to an excellent R -factor of 5.7% and a χ^2 of 1.05 from the starting parameters given by Shoemaker *et al* (1977). The result of this refinement is also tabulated in table 1. The cell dimensions of our sample at ambient temperature are

$$\begin{aligned} a &= 4.855(1) \text{ \AA} & b &= 5.288(1) \text{ \AA} & c &= 6.184(1) \text{ \AA} \\ \alpha &= 72.34(1)^\circ & \beta &= 86.99(1)^\circ & \gamma &= 68.54(1)^\circ. \end{aligned}$$

The low-temperature data were limited due to lack of experimental time and were

Table 1. The atomic positional and thermal parameters for triclinic $\text{Cu}_3(\text{PO}_4)_2$. For each atom, the first row gives the values from the ambient temperature single-crystal x-ray diffraction study by Shoemaker *et al* (1977). Second row: ambient temperature neutron powder diffraction; third row: 15 K single-crystal neutron diffraction to $\sin \theta/\lambda = 0.48 \text{ \AA}^{-1}$ (isotropic temperature factors only). The positional parameters are given in 10^{-4} of the cell dimensions; the estimated standard deviations are included in parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B11	B22	B33	B12	B23	B13
Cu1	0	0	0	0.81(2)	0.94(2)	1.31(2)	-0.36(2)	-0.22(2)	-0.15(2)
	0	0	0	0.54(6)					
	0	0	0	0.40(10)					
Cu2	2776(1)	2258(1)	3157(1)	0.97(2)	1.28(2)	0.97(2)	-0.14(1)	-0.47(1)	-0.12(1)
	2771(5)	2259(5)	3149(4)	0.56(4)					
	2779(7)	2265(6)	3155(6)	0.55(9)					
P	3586(2)	3534(2)	7785(2)	0.69(3)	0.87(3)	0.89(3)	-0.27(2)	-0.26(2)	-0.06(2)
	3563(6)	3553(6)	7756(6)	0.14(6)					
	3590(11)	3538(10)	7774(8)	0.50(11)					
O1	-1536(6)	3443(6)	3389(5)	0.95(9)	1.06(9)	1.16(9)	-0.24(7)	-0.14(7)	-0.08(7)
	-1548(6)	3436(6)	3408(5)	0.61(6)					
	-1557(10)	3461(9)	3403(7)	0.68(10)					
O2	3324(6)	6515(6)	1695(5)	0.90(9)	1.13(9)	1.36(9)	-0.45(7)	-0.38(7)	-0.03(7)
	3341(6)	6539(6)	1701(5)	0.42(5)					
	3304(10)	6531(9)	1720(7)	0.61(10)					
O3	2303(6)	2274(6)	49(5)	0.99(9)	1.16(9)	0.92(9)	-0.42(7)	-0.48(7)	0.11(7)
	2310(6)	2269(6)	49(5)	0.39(6)					
	2314(9)	2260(8)	49(10)	0.50(10)					
O4	3786(6)	1498(6)	6334(5)	1.02(9)	1.01(9)	0.99(9)	-0.17(7)	-0.48(7)	-0.19(7)
	3752(6)	1504(6)	6342(5)	0.32(6)					
	3769(10)	1520(9)	6343(7)	0.53(10)					

confined to the large *d*-spacings where any magnetic peaks would be strongest. Although the use of back-scattering implies that such large *d*-spacings can only reflect long-wavelength neutrons, for which the incident intensities are weak, we were able to observe three new peaks of magnetic origin which could be indexed as $(11\frac{1}{2})$, $(10\frac{1}{2})$ and $(00\frac{3}{2})$ on the chemical cell. Although these peaks suffice to show that the magnetic propagation vector is probably $(00\frac{1}{2})$, the weakness and paucity of the magnetic reflections precluded any structure determination. The low-temperature nuclear scattering showed that the crystal structure of $\text{Cu}_3(\text{PO}_4)_2$ remains essentially unchanged down to liquid helium temperatures. The cell dimensions at 6 K are

$$\begin{aligned}
 a &= 4.848(1) \text{ \AA} & b &= 5.280(1) \text{ \AA} & c &= 6.183(1) \text{ \AA} \\
 \alpha &= 72.30(1)^\circ & \beta &= 86.90(1)^\circ & \gamma &= 68.59(1)^\circ.
 \end{aligned}$$

3. Single-crystal diffraction

Several crystals selected from one of the first batches of sample produced were examined using the TOF single-crystal diffractometer (SCD) at the IPNS pulsed spallation source at the Argonne National Laboratory, USA. These crystals were less than 5 mg in weight

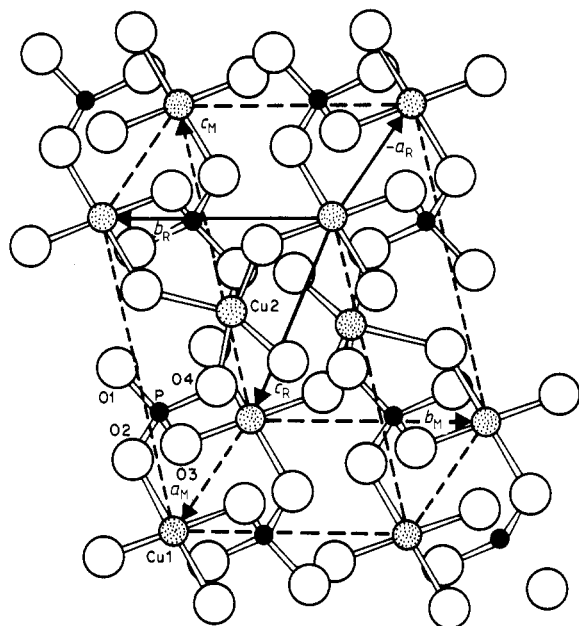


Figure 2. The unit cell of $\text{Cu}_3(\text{PO}_4)_2$ following Shoemaker *et al* (1977). The axes of the triacute reduced cell ($-a_R$, b_R , c_R) are shown by bold lines. The morphologically significant unit cell (a_M , b_M , c_M) is shown with broken lines.

and all proved to be twinned: the two twin components were of roughly equal weight and were related to each other by rotation about b^* . The lowest temperature that could be reached at that time using a two-stage Joule–Thompson cooler was 20–30 K, but no additional peaks of magnetic origin were seen in the two-dimensional position-sensitive detector on reaching base temperature.

Subsequently, some slightly larger crystals were selected from a later hydrothermal synthesis which seemed to have produced many more crystals that were not obviously twinned to produce ‘butterfly’ intergrowths. All showed six well-developed faces corresponding to the principal planes of the morphological unit cell described by Shoemaker *et al* (1977) (figure 2). A 6.2 mg crystal with edges approximately $2 \times 1.3 \times 1 \text{ mm}^3$ was mounted parallel to its longest edge and transferred to the D15 single-crystal diffractometer at the Institut Laue–Langevin, Grenoble, France. The chosen orientation had [100] of the crystallographic cell as the rotation axis in the normal-beam, zero- and higher-layer geometry of the instrument. After cooling to 4 K in an ILL Orange liquid helium cryostat and refining the crystal orientation matrix, several $(0kl)$ reflections with half-integer l were quickly located, confirming the existence of the magnetic propagation vector $(00\frac{1}{2})$ deduced from the powder experiment. No reflections that would be produced by twinning of the sort described above were found, nor could further magnetic peaks be found at other rational fractional indices. However, some extra scattering was seen in the form of extended peaks but no systematic prescription for their occurrence could be found. We presume that this extra scattering came from one or more additional components in our crystal, related to the major component by random reorientations.

Routine data collection was carried out at 2.0 K, measuring magnetic peaks with $h = -1, 0$ and 1 out to a $\sin\theta/\lambda$ limit of 0.48 \AA^{-1} , together with 20 nuclear peaks to scale the magnetic intensities and including four to act as standards. Figure 3 shows the

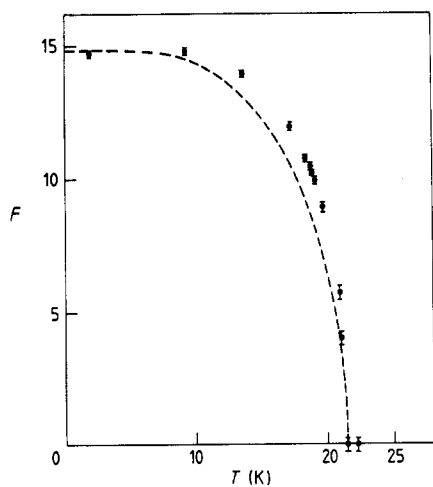


Figure 3. The temperature dependence of the modulus of the $(00\frac{1}{2})$ magnetic interaction vector measured on D15: a Néel point of 21.4(3) K is indicated. The broken curve corresponds to the Brillouin function for $S = \frac{1}{2}$.

temperature dependence of the modulus of the strong $(00\frac{1}{2})$ magnetic interaction vector as a function of temperature: a Néel temperature of 21.4(4) K is indicated, which is rather lower than that suggested by the susceptibility data (figure 1). As a precaution against the integrated intensities containing any contributions from a second crystal component, their intensities were remeasured at 30 K, well above the ordering temperature. Peaks that still had significant intensity at the higher temperature were not included in the structure determination.

Finally, the crystal was remounted about $[0-10]$, parallel to its 1.3 mm edge, and magnetic intensities collected to the same limit in $\sin \theta/\lambda$ for reflections with $k = -1, 0$ and 1. A limited number of nuclear reflections were again measured to provide a scale and the intensities of the magnetic peaks were again remeasured at 30 K.

4. The magnetic structure at 2 K

The small volume of the largest single crystal available to us, and the need to discount several magnetic peaks due to their contamination by nuclear scattering from minor crystal components, reduced the final number of unique magnetic reflections to 38 of a possible 260 inside the $\sin \theta/\lambda$ measurement limit of 0.48 \AA^{-1} . However, the major reason for rejection was a lack of significant observed intensity. After correction for the diffraction geometry, the observed values of the magnetic interaction vector were placed on an absolute scale by reference to the measured nuclear structure factors. The latter were in excellent agreement ($R = 0.042$) with those calculated for the ambient temperature structure, since they were at low $\sin \theta/\lambda$ and not much affected by any reduction in the atomic temperature factors. Absorption is negligible in such a small crystal.

For the Cu1 atom at the inversion centre in the crystal structure to exhibit a moment requires that the centre does not involve time reversal. As a consequence, we should also expect the moments of the two Cu2 ions related by this centre to be parallel. The magnetic Patterson approach of Wilkinson (1968, 1973) was used to obtain a starting orientation for the Cu1 and Cu2 moments, prior to a least-squares refinement of their

Table 2. The observed, F_o , and calculated, F_c , moduli of the magnetic interaction vectors in $\text{Cu}_3(\text{PO}_4)_2$. The estimated standard deviations of the observed values are given in parentheses. The units must be multiplied by the experimentally determined scale factor of 0.0348 to convert them to Bohr magnetons.

h	k	l	F_o	F_c	h	k	l	F_o	F_c
-1	-2	0.5	10.00(30)	9.71	-1	1	1.5	4.73(19)	5.48
0	-2	0.5	3.60(40)	3.58	0	1	1.5	4.75(14)	5.38
-2	-1	0.5	8.87(20)	9.48	1	1	1.5	5.46(15)	4.41
-1	-1	0.5	8.89(10)	9.97	2	1	1.5	2.19(110)	4.00
0	-1	0.5	2.97(29)	2.72	-1	2	1.5	2.28(66)	1.28
2	-1	0.5	6.20(37)	5.58	0	2	1.5	2.90(39)	1.36
-1	0	0.5	2.32(46)	1.69	1	3	1.5	7.17(35)	6.35
0	0	0.5	0.86(75)	0.49	0	-1	2.5	9.77(22)	9.62
0	1	0.5	2.99(25)	4.45	-2	0	2.5	2.04(79)	2.21
0	2	0.5	3.50(30)	4.08	-1	0	2.5	10.85(11)	10.84
1	0	0.5	10.62(9)	11.01	2	0	2.5	5.68(32)	5.85
2	0	0.5	4.60(60)	4.39	0	1	2.5	3.42(29)	3.55
2	1	0.5	4.54(41)	3.39	1	1	2.5	5.07(35)	6.04
-2	-1	1.5	5.73(34)	6.10	1	0	3.5	6.69(34)	7.32
-1	-1	1.5	4.00(29)	4.08	0	1	3.5	6.49(17)	6.20
0	-1	1.5	3.52(48)	3.69	1	1	3.5	8.20(30)	8.28
1	-1	1.5	8.45(19)	8.38	0	2	3.5	7.14(35)	6.91
-2	0	1.5	2.57(37)	2.17	0	0	4.5	7.00(35)	6.87
0	0	1.5	14.51(7)	14.23	0	1	4.5	5.60(50)	5.58

magnitudes and orientations using MAGLSQ, a member of the Cambridge Crystallographic MK3 suite of subroutines and programs (Brown and Matthewman 1987). A refinement of the six variables that define the magnitude and orientation of the magnetic moments on both Cu sites resulted in a weighted R -factor, R_w , of 0.069, with similar moment values and moment directions which were within 15° of being antiparallel. The magnetic form factor used was derived from the Hartree-Fock wavefunctions for the free Cu^{2+} ion given by Clementi and Roetti (1974). The observed magnetic intensities were systematically higher than those calculated at the higher values of $\sin \theta/\lambda$. The possibility that the true form factor might have a different radial dependence than that corresponding to the free ion was then allowed for by refining a contribution to the radial form factor with the angular dependence of the associated $\langle j_2 \rangle$ radial integral (Watson and Freeman 1961): this lowered R_w to 0.054. Constraining the moments to be equal in magnitude gave a refinement to $R_w = 0.057$ with six variables and a refinement that also constrained the moments to be antiparallel (four variables) gave a final R -factor of 0.087 with $\chi^2 = 9.7$ and $R_w = 0.060$. No significant reorientation of the moments occurred between the last two refinements and we conclude that, within the accuracy of our observations, the magnetic structure is collinear with the Cu1 moment having angles of $\theta = 72(2)^\circ$ and $\varphi = 135(2)^\circ$, the Cu2 moments being antiparallel; here θ and φ are the polar angles referred to the orthogonal crystal axes with [001] as the polar axis (z) and x along a^* . The φ -angles are measured from the x, z plane. The Cu^{2+} moments are $0.68(1) \mu_B$ with a radial expansion of 14(3)%. Table 2 lists the moduli of the observed magnetic structure factors, their standard deviations and the values calculated for the above model.

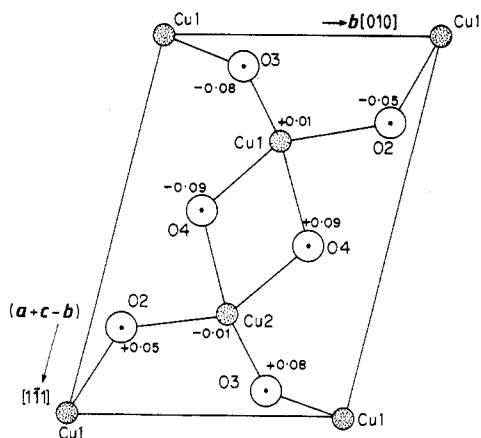


Figure 4. The antiferromagnetic exchange paths linking Cu1 and Cu2 ions lying in approximately (-101) sheets in the structure of $\text{Cu}_3(\text{PO}_4)_2$. The Cu2, O2, O3 and O4 atoms have been projected onto the plane down $[-201]$, an approximate normal to the plane. The numbers against these atoms are their fractional coordinates out of the plane parallel to this 11.5 Å axis.

We were subsequently able to use the D9 diffractometer fitted with a limited area position-sensitive detector (Lehmann *et al* 1989) to integrate and investigate the intensity profiles of the reflections in more detail than was possible with the single detector on D15. Although the nuclear reflection data again refined well to $R_w = 0.038$ and structural parameters close to those at ambient temperature, the much weaker magnetic reflections produced essentially the same fit to the magnetic structure model produced from the D15 data. No significant improvement in fit to the nuclear data was obtained by allowing the oxygen atoms to have anisotropic temperature factors; the final parameters for the structure at 15 K are included in table 1.

5. Discussion

The magnetic exchange paths in $\text{Cu}_3(\text{PO}_4)_2$ are antiferromagnetic in character and link the copper ions via their common oxygen ligands, with bond distances of around 2 Å, lying approximately in (-101) sheets (figure 4). A Cu2 atom is linked to a Cu1 atom via an O3, with the angle at O3 being 109.3° and, more weakly, to a second Cu1 via O2 with an angle of 121.9° at O2. Cu2 atoms are linked to each other via two O4 atoms with an included angle at O4 of 98.2° . The exchange paths which link successive (-101) sheets pass through the phosphate group, the Cu–O–P–O–Cu triple exchange being quite effective as was first pointed out by Mays (1963), as has also been noted in other phosphates such as $\text{Co}_3(\text{PO}_4)_2$ (Forsyth *et al* 1988b). The shortest Cu–Cu distance is 3.00 Å, between Cu2 and Cu2, so direct exchange makes little or no contribution to the stability of the magnetic structure. Overall, the magnetic coupling produces a collinear magnetic structure since the orbital moment of Cu^{2+} is weak, even in a strong tetrahedral field. This is in contrast to the pronounced non-collinearity exhibited by cobalt ortho- and di-phosphates (Forsyth *et al* 1988b, 1989) in which the Co^{2+} ion carries a large orbital moment. Figure 5 shows the relationship of the Cu^{2+} moment directions to those of the ligand oxygen atoms.

The difference of some 9 K between the temperature at which the inverse susceptibility is a minimum and the Néel temperature obtained from the D15 neutron diffraction measurements is rather large. This difference is removed, however, if the Néel point is estimated from the inflection point below the temperature at which the

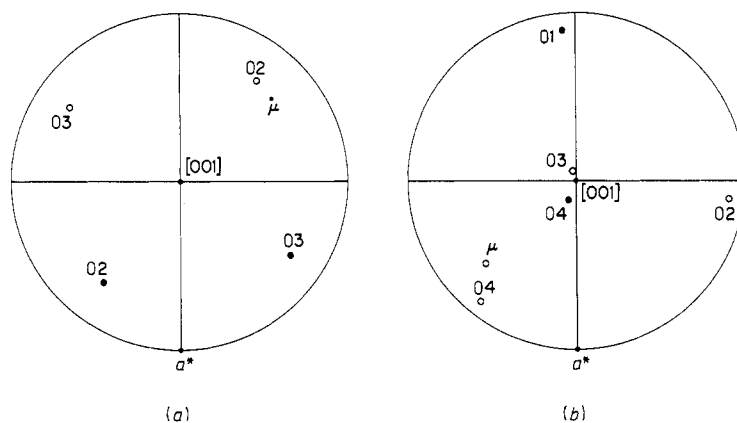


Figure 5. Stereograms showing the orientation of the Cu^{2+} moments with respect to their oxygen ligands for (a) Cu1 and (b) Cu2.

susceptibility is a maximum. A second measurement using the D9 diffractometer gave a Néel point at 23.0(5)K, so we take 22.2(5) K as our best estimate. The position of the minimum in the observed susceptibility could result from an additional contribution by a second magnetic phase with a higher transition temperature, however, no evidence for an impurity phase was found in the neutron powder data. Although the temperature dependence of the $(00\frac{3}{2})$ reflection lies above the Brillouin curve appropriate to spin $\frac{1}{2}$ (see figure 3), there is no discontinuity in its slope; in CuO, the transition from commensurate to incommensurate magnetic order some 17 K below its Néel temperature is clearly seen as an abrupt fall in the temperature dependence of the intensities of magnetic reflections from the commensurate phase (Forsyth *et al* 1988a). We therefore conclude that the temperature of 22.2(5) K is associated with the antiferromagnetic-paramagnetic transition.

When the present experimental work had been completed, we found that a recent paper on the solid solution of $(\text{Mg}, \text{Cu})_3(\text{PO}_4)_2$ by Moqine *et al* (1987) contained magnetic susceptibility data on powdered $\text{Cu}_3(\text{PO}_4)_2$. These authors report a maximum in the susceptibility at 40 K, even higher than our own result. In their discussion of the exchange paths in the structure, they discount the interaction between (-101) sheets of Cu atoms and also conclude that exchange within the sheet that involves O2 is likely to be so weak as to effectively limit the magnetic coupling to the chains of Cu2–Cu1–Cu2 trimers running parallel to $[101]$. Our results, however, clearly establish the three-dimensional character of the magnetic order. The relatively low precision and paucity of our magnetic data, due to the low moment and small crystal size, preclude any meaningful attempt to model the magnetisation density at the Cu^{2+} sites by a multipolar expansion of the type used in the study of CuO (Forsyth *et al* 1988a); we therefore have no experimental information about the occupancies of the $d_{x^2-y^2}$ and d_{z^2} orbitals of the d^9 copper ions in their strongly distorted environments resulting from the Jahn–Teller effect. The magnitude of the Cu^{2+} moment of $0.68(1) \mu_B$ is similar to that of $0.65(3) \mu_B$ found in CuO (Forsyth *et al* 1988a); a reduction from the free ion value of $1 \mu_B$ of at least 10% is to be expected due to the zero-point spin deviation in antiferromagnets (see, for example, Lovesey 1984) and some further reduction will occur due to covalent spin transfer to the ligands. A radial expansion of the observed Cu^{2+} magnetic form factor

compared to that for the free ion was also observed in CuO , where it amounted to some 9%.

Acknowledgments

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