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The antiferromagnetic structure of copper tungstate, CuWO_4

J B Forsyth†, C Wilkinson‡ and A I Zvyagin§

† ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Oxon OX11 0QX, UK

‡ Physics Department, King's College (KQC) The Strand, London WC2R 2LS, UK

§ Institute of Low Temperatures, Ukrainian Academy of Sciences, Kharkov, USSR

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Abstract. Copper tungstate becomes antiferromagnetically ordered below 23.0(2) K and its magnetic structure has been determined from single-crystal unpolarized neutron diffraction measurements at 5 K. The chemical unit cell is triclinic $P\bar{1}$, with $a = 4.694(1)$, $b = 5.830(1)$, $c = 4.877(1)$ Å, $\alpha = 91.64(1)$, $\beta = 92.41(2)$ and $\gamma = 82.91(1)^\circ$ at 15 K. The magnetic propagation vector is $(\frac{1}{2}00)$ and the magnetic space group $P2_1a\bar{1}$. The two equivalent copper ions within the unit cell have magnetic moments of $0.67(1) \mu_B$ aligned ferromagnetically at the spherical polar angles $\Theta = 121(2)^\circ$ and $\phi = 52(2)^\circ$, the polar axis being parallel to c and ϕ being measured from the c - a^* plane. This direction coincides, within experimental error, with the axis of elongation of the Jahn-Teller distorted octahedron of oxygen atoms about the Cu^{2+} ion. A multipole refinement of the moment distribution, to order two on quantum axes Z parallel to the moment direction and X, Y directed towards the four close oxygen neighbours, shows that $Y20$ is the only significant multipole. Its sign indicates that the moment distribution approximates to an oblate ellipsoid of revolution with its axis parallel to Z . Only two of the six oxygen neighbours of the Cu^{2+} ion carry a significant transferred moment of $0.06(1) \mu_B$. These observations are related to the exchange paths and covalency in the compound.

1. Introduction

The magnetic behaviour of oxygen-coordinated copper in the nominally divalent state has been the subject of much recent interest since it is found that both octahedral and square-planar coordinated ions occur in the high- T_c superconductors. In those structures which exhibit antiferromagnetism, the copper moment found by neutron diffraction is around $0.6 \mu_B$ which is lower than that associated with purely ionic Cu^{2+} . A similar moment is found in the low temperature collinear magnetic phase of cupric oxide itself (Forsyth *et al* 1988). In that single crystal neutron study, the authors concluded that the wavefunctions describing the magnetic hole were not confined to a single $d_{x^2-y^2}$ orbital in the plane of the square-planar coordination. In addition, evidence was found for the covalent transfer of moment to the ligand oxygen atoms, each of which has three copper neighbours.

We now describe a study of copper tungstate which, like CuO , exhibits a strong Jahn-Teller distortion to square-planar coordination. The effect on the structure is

† Now at EMBL, BP 156 Grenoble 38402 Cedex France.

to lower the symmetry from monoclinic, found in the wolframite structure of the Mn, Co, Fe and Ni tungstates, to triclinic $P\bar{1}$ (Kihlberg and Gebert 1970). The whole series exhibits long-range antiferromagnetic order at low temperatures and in each case the propagation vector has been established as $(\frac{1}{2}00)$ by powder neutron diffraction (Weitzel 1970). Single crystal neutron studies of the Co and Ni tungstates (Wilkinson and Sprague 1975) confirmed the propagation vector as $(\frac{1}{2}00)$ and established an accurate moment direction for NiWO_4 . The magnetic structure of CuWO_4 has, however, remained ill-defined, since the copper moment is low and the earlier powder study was made with an instrumental resolution insufficient to resolve properly even the high d -spacing diffraction lines from the triclinic cell.

2. Experimental details

The first neutron diffraction experiments were performed with the largest single crystal from a batch produced at the Clarendon Laboratory, Oxford, using a flux growth technique (Wanklyn and Garrard 1983). These crystals formed as needles elongated along [001] and had a silver-grey metallic lustre. Unfortunately, the crystal only weighed 14 mg and had dimensions $5 \times 0.6 \times 0.6$ mm. Neutron diffraction measurements were made at the Institut Laue Langevin, Grenoble using both the D9 and D15 diffractometers. Integrated intensity data taken at 15 K on the former instrument showed that the crystal structure remained essentially unchanged from that at room temperature. D15 integrated intensity data for the $\{hk0\}$ and $\{hkl\}$ layers of reflections, with the sample rotating about [001] in an ILL 'Orange' liquid helium cryostat data at 4 K, confirmed that the magnetic propagation direction was indeed $(\frac{1}{2}00)$ as described by Weitzel (1970). However, the intensities of all but a few magnetic reflections were too weak to obtain reasonable accuracy in the magnetic structure factors.

A more detailed study of the magnetization was then made using D15 and a much larger crystal grown at the Laboratory of Low Temperature Physics of the Ukrainian Academy of Sciences, Kharkov USSR, using the Czochralski technique. This crystal had the form of a plate, 0.8 mm thick, cut perpendicular to b^* with dimensions 4×2 mm parallel to [001] and [100], respectively. The fundamental reflections have no magnetic content and $\{0kl\}$ data were measured out to a $\sin \Theta/\lambda$ limit of 0.75 \AA^{-1} , with the crystal rotated about [100], to establish the parameter describing the small degree of extinction in the crystal and the scale. These data showed excellent agreement between the Friedel pairs. The magnetic reflections, which have half-integral h indices, are generally weak and the $\{-\frac{1}{2}k1\}$, $\{\frac{1}{2}k1\}$ and $\{1\frac{1}{2}k1\}$ layers were measured at 25 minutes/reflection out to $\sin \Theta/\lambda$ 0.55 \AA^{-1} , using the normal-beam, lifting detector geometry of D15. The crystal was then remounted about [001] and the magnetic reflections measured in the zero and first layers to the same limit in $\sin \Theta/\lambda$. In addition, some zero-layer nuclear reflections were measured as a more sensitive check on the agreement between equivalent reflections and the reliability of the path-length-dependent extinction correction. A total of 457 nuclear and 471 magnetic reflections were averaged over Friedel pairs to give 326 and 283 independent moduli of structure factors, respectively.

The temperature dependence of the strongest magnetic reflection, $(\frac{1}{2}00)$, is illustrated in figure 1 which shows that the Néel point occurs at 23.0(2) K, in good agreement with the temperature of 24 ± 1 K established from the disappearance of EPR signals by Anders *et al* (1972). This temperature is considerably lower than the

90 K reported by Weitzel from his powder neutron study, but this latter temperature does correspond to a broad maximum in the magnetic susceptibility of the material shown in figure 2.

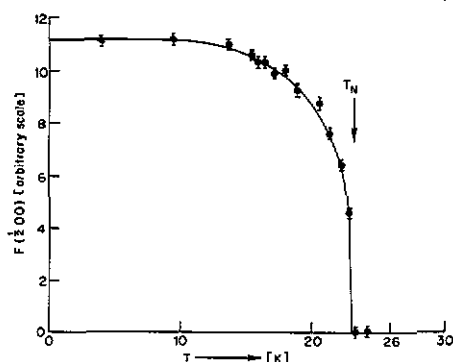


Figure 1. The temperature dependence of the magnetic $(\frac{1}{2}00)$ reflection from CuWO_4 , showing a Néel temperature of 23.0(2) K. The full curve is a guide for the eye.

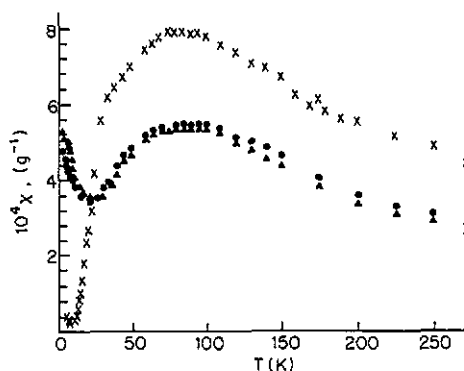


Figure 2. The temperature dependences of the magnetic susceptibilities of single crystal CuWO_4 : \times parallel to b , \bullet and \blacktriangle in the plane perpendicular to b at angles of $\pm 45^\circ$ to c (Anders *et al* 1972).

3. Refinement of the crystal structure at low temperature

The nuclear data collected from the small crystal on D9 showed excellent agreement between Friedel pairs, and a least squares refinement starting from the room temperature positional parameters reported by Kihlberg and Gebert (1970), allowing only isotropic temperature factors, led to an agreement factor R ($R = \sum |F_0 - F_c| / \sum F_c^2$) of 7.1%, a weighted R_w of 6.6% and a χ^2 of 178 for 26 variables and 784 independent

reflections. The estimated standard deviations, σ , of the observed structure factors were obtained from the agreement between Friedel pairs or the counting statistics, whichever was the greater, and the weighting was $1/\sigma^2$. A small degree of extinction was evident in the strongest reflections, so this was modelled using the Becker-Coppens treatment, introducing a Lorentzian distribution of mosaic spread with a fixed domain radius (Becker and Coppens 1974). The subsequent refinement produced a final R factor of 3.3%, $R_w = 2.6\%$ and $\chi^2 = 16$ for 27 variables and 784 reflections. No significant improvement was obtained by allowing the oxygen atoms to have anisotropic temperature factors. The fractional atomic coordinates, isotropic temperature factors and their estimated standard deviations from the refinement are listed in table 1 together with the room-temperature x-ray values obtained by Kihlberg and Gebert. The positional parameters are little changed in going to 4 K; the neutron parameters are less accurate for tungsten, about equivalent for copper and some five times better for oxygen than those from the x-ray study, as would be expected. Room temperature neutron powder data have been used by von Klein and Weitzel (1975) as a test of their PERNOD refinement program, but their final parameters are generally much less accurate than those found in the single crystal x-ray study. Figure 3 illustrates the chemical structure of the compound.

Table 1. The atomic positional and thermal parameters in CuWO_4 at 4 K (first line) compared to those at room temperature (Kihlberg and Gebert 1970). The isotropic thermal vibration parameters, ITF, are in units of \AA^2 .

	x	y	z	ITF
Cu	0.49537(13)	0.65942(11)	0.24524(14)	0.169(9)
	0.49533(16)	0.65976(13)	0.24481(15)	
W	0.02146(22)	0.17353(17)	0.25405(22)	0.096(13)
	0.02106(4)	0.17348(3)	0.25429(4)	
O1	0.25042(18)	0.35475(15)	0.42520(20)	0.282(12)
	0.2491(10)	0.3535(8)	0.4245(10)	
O2	0.21551(18)	0.88077(15)	0.42901(20)	0.236(12)
	0.2145(10)	0.8812(7)	0.4309(9)	
O3	0.73511(18)	0.38077(15)	0.09822(20)	0.269(12)
	0.7353(10)	0.3803(8)	0.0981(9)	
O4	0.78214(19)	0.90774(15)	0.05459(20)	0.266(12)
	0.7826(9)	0.9079(8)	0.0533(9)	

4. Determination of the magnetic structure

The two magnetic data sets from the large crystal contained 37 unique reflections in common and these were used to merge the two data sets with a scale factor of 1.039, which presumably reflected a small difference in the incident beam characteristics within the area sampled by the crystal in its two different mountings. A large fraction of the measured reflections contained no significant intensity and were removed from the final data set of 164 unique reflections. A magnetization density Patterson section (Wilkinson 1973) at $z = 0.5104$ clearly showed that the moments on the two Cu^{2+} within the chemical unit cell are predominantly ferromagnetically coupled. The same

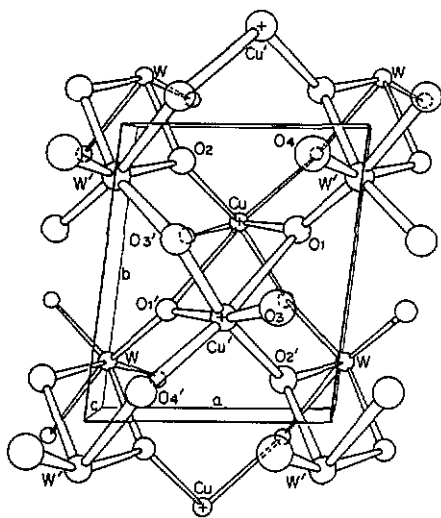


Figure 3. The structure of copper tungstate: the labelling of the atoms corresponds to that of table 1. Primed atoms are related to the corresponding unprimed ones by a centre of inversion.

ferromagnetic coupling is also found between the two transition metal moments in the related structures of FeWO_4 , CoWO_4 and NiWO_4 . The elongation of the Patterson peak suggested that the Cu^{2+} moment was inclined at some 45° to the c - a^* plane in that section. The orientation of the moment component within that plane indicated in the Patterson section at $y = 0.6812$ was around 110° to c in β obtuse. Refinement of the D15 magnetic data from these starting angles and using a spherical form factor calculated from the Cu^{2+} free atom wavefunctions of Clementi and Roetti (1974), produced a reasonable fit with $\chi^2 = 28$ when the moments on the two copper ions within the chemical unit cell are coupled ferromagnetically with a moment of $0.67(1) \mu_B$ and a spin direction $\Theta = 121(2)^\circ$ and $\phi = 52(2)^\circ$. Here Θ and ϕ are the spherical polar angles relative to the orthogonal crystallographic axes, with Θ being measured from $[001]$ and ϕ from the plane containing $[001]$ and a^* . The R factor was 21.9%, with $R_w = 15.1\%$ for the three variables and 164 independent reflections. The high value for R is partly due to the large fraction of weak data: reducing the data to the 70 stronger reflections gave much better agreement, $R = 11.5\%$, $R_w = 9.1\%$, but produced no significant change in the magnitude of the moment or its orientation. Figure 4 shows a stereographic projection of the oxygen ligand directions about the Cu^{2+} ion, from which it can be seen that the magnetic moment direction coincides with the direction of elongation of the oxygen octahedron produced by the Jahn-Teller effect.

The relatively poor overall R factor and high value of χ^2 led us first to test whether the centre of inversion was retained in the magnetic structure. A refinement starting from Cu^{2+} moment directions some 40° apart converged to parallelism within the estimated accuracy of 5° , supporting the retention of $P\bar{1}$ symmetry. A further test was made in which the moment was confined to the c - a^* plane, as it is in the monoclinic tungstates of Mn, Fe, Co and Ni. This refinement produced values for both R and R_w which were roughly twice those obtained above, convincingly demonstrating that that moment orientation is not correct. The improved modelling of the neutron data by a multipole expansion of the Cu moment obtained by Forsyth *et al* (1988) in their study of CuO encouraged us to try the same technique on the CuWO_4 data and to test for the presence of moment on the oxygen ligands of Cu^{2+} resulting from covalent

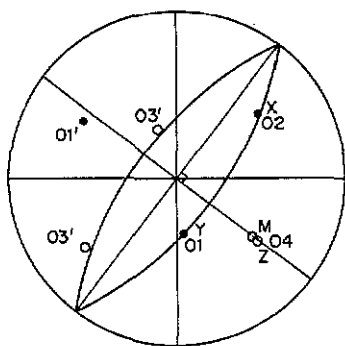


Figure 4. Stereogram showing the direction M of the copper magnetic moment with respect to the neighbouring oxygen atoms. $O1$, $O2$, $O3$ and $O3'$ form the distorted square planar coordination at an average distance of 1.98 \AA ; atoms $O4$ and $O1'$ are at 2.34 and 2.45 \AA , respectively. The atom labelling corresponds to that of table 1. The primed atoms are related to the unprimed ones by a centre of inversion. The moment is found to lie parallel to the direction $Cu-O4$.

transfer. Although the site symmetry of Cu is $P1$, which places no limitation on the order of multipoles which could be used to model the moment, the six oxygen ligands approximate to tetragonal symmetry so the Z quantum axis for Cu^{2+} was taken parallel to the moment direction, the tetrad axis, with X and Y approximately in the directions of the four close oxygen neighbours. The arrangement is roughly centrosymmetric so only multipoles Ylm with even $l = 0, 2$ and 4 were considered. Unfortunately, the more accurate experimental data did not extend far enough in $\sin \Theta/\lambda$ to determine the amplitudes of multipoles with $l = 4$ with any precision, but a least-squares refinement showed conclusively that only the $Y20$ multipole of order 2 had significant amplitude and that one of the oxygen ligands, $O3$, carried a significant net moment of $0.06(1) \mu_B$ parallel to that on Cu^{2+} . The radial dependence of the Cu^{2+} form factor also appears to be expanded relative to that corresponding to the free-atom wavefunctions by some 13% in the $\sin \Theta/\lambda$ range of the measurements.

5. Discussion

The sign of $Y20$ in our multipole refinement is consistent with the accepted orbital scheme for Cu^{2+} in a pseudo-tetragonal environment in which the E_g hole states are lower and the single hole is in a $d_{x^2-y^2}$ orbital which points to the ligands in the square plane. This is in contrast to the situation in CuO , where the neutron data were consistent with an equal occupation of the $d_{x^2-y^2}$ and d_{xz} orbitals. The appearance of a transferred moment of $0.06(1)$ on the $O3$ atoms is probably due to the short distance they make to a pairs of ferromagnetically ordered Cu ions in the zig-zag chains. Its magnitude is, however, less than the $0.14(4) \mu_B$ found on the oxygen atoms in CuO (Forsyth *et al* 1988).

Although Anders *et al* (1972) measured the magnetic susceptibility of their single crystal samples along their three magnetic axes, as shown in figure 2, these axes were

chosen with reference to the monoclinic symmetry of the related structure adopted by the Mn, Fe, Co and Ni tungstates, z being along b and x and y lying in the a - c plane at $\pm 45^\circ$ to c . The pronounced anisotropy does, however, indicate the importance of single ion anisotropy and this is borne out by our observation that the Cu^{2+} moments are aligned along the axis of the Jahn-Teller distortion. The temperature dependence of the susceptibility above the Néel point mimics that found in CuO , which exhibits a maximum in its susceptibility at 500 K, again well above its T_N of 230 K. In both cases it would appear that considerable short range antiferromagnetic order persists well above the temperature at which long-range order is lost. In CuWO_4 , the analysis of the EPR spectra from $\text{ZnWO}_4\text{-Cu}^{2+}$ containing 0.5 10% Cu by Anders *et al* (1972) gave an estimate for the antiferromagnetic exchange integral of some 30 K, in reasonable agreement with the Néel temperature. The broad maximum in the susceptibility at around 90 K must therefore be associated with a stronger antiferromagnetic coupling which does not, however, lead to long-range order.

The magnetic exchange paths in the wolframite structure have been discussed by Weitzel and Langhof (1977) in relation to the magnetic structures of the Mn, Fe, Co and Ni tungstates. The related crystal structure of CuWO_4 can be thought of as pseudo-hexagonal nets of oxygen atoms in the b - c plane. The cations alternate Cu, W, Cu, ... parallel to a and are accommodated between the oxygen planes to form infinite zig-zag chains of edge-linked polyhedra extending parallel to c as shown in figure 5. It is clear that the antiferromagnetic exchange interactions associated with the onset of short range order around 90 K, and then long-range order with the magnetic axis $a' = 2a$, must result from Cu-O-(W)-O-Cu triple exchange paths of the type first invoked by Mays (1963) to account for the magnetic structure of LiMnPO_4 . Table 2 lists the only such pathways in which the angles at both intervening oxygen atoms are greater than 110° , the second and third of them being centrosymmetric. Both the bond angles and bond lengths suggest that the second path, via O2, should provide the strongest antiferromagnetic coupling, particularly since the two O2 atoms form an edge common to two WO_6 octahedra. If this is so, the Cu-Cu' pairs could be responsible for the short range order observed below 90 K. Interaction via the third path would link the antiferromagnetic pairs to form chains along $[201]$ and, via the first path, produce long-range order. It should be possible to locate the diffuse scattered neutron intensity produced by the short range order if a larger single crystal were available.

Table 2. The angles at the oxygen atoms and the bond lengths in the strong antiferromagnetic triple exchange paths in CuWO_4 . Primed atoms lie within the reference unit cell at positions related by a centre of inversion to those of the unprimed atoms of table 1. Atom $[UVW]$ is located in the cell whose origin is displaced by $Ua + Vb + Wc$ from the origin of the reference cell.

(1)	Cu	—	159.2°	—	154.6°	Cu [100]
		1.960 Å	O1'	2.833 Å	O3' [100]	
(2)	Cu	—	165.4°	—	165.4°	Cu' [110]
		1.955 Å	O2	2.423 Å	O2' [110]	
(3)	Cu	—	160.5°	—	160.5°	Cu' [111]
		2.332 Å	O4	2.522 Å	O4' [111]	

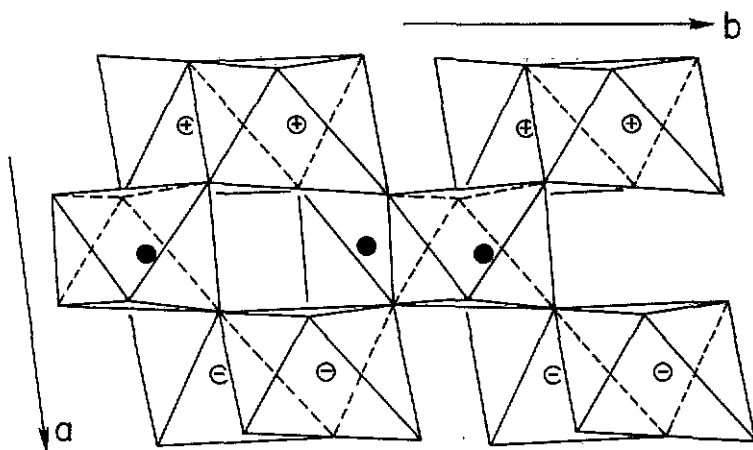


Figure 5. The structure of CuWO_4 shown as linked octahedra viewed along c . Open and full circles represent Cu and W atoms respectively, and the + and - signs on the Cu atoms show the antiferromagnetic configuration.

The Cu ions in their infinite chains are alternately linked through a pair of O3, O3' atoms forming part of the square planar coordination and resulting in a Cu-Cu' distance of $2.986(2)$ Å, then through a pair of O1 atoms, one in the square plane and the other an apical atom: the Cu'-Cu distance in this case is $3.150(2)$ Å. In both these instances the resultant coupling Cu-O-Cu' is through $\sim 97^\circ$ superexchange and must be weak, as is also the case for Cu-O-Cu coupling within the Cu-O ribbons in CuO in which adjacent Cu ions share two oxygen ligands: in both CuO and CuWO_4 the stronger antiferromagnetic exchange interactions are dominant and the moments of the Cu ions in the ribbons and zig-zag chains are aligned ferromagnetically as a result of stronger, antiferromagnetic inter-chain interactions.

Acknowledgments

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