On covalence in anhydrous copper (II) sulphate from polarized neutron diffraction

Philip A Reynolds and Brian N Figgis

School of Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia

Abstract. Existing polarized neutron diffraction data on anhydrous copper sulphate has been reanalysed. Covalence of about 23(5)% is observed. The spin is delocalized predominantly along the shortest Cu–O(3) bond, reaching the S atom. This provides a pathway for the antiferromagnetic interaction. The copper site configuration in this Jahn–Teller distorted ion, with two bonds much longer than the remaining four, is dominated by the population in the $3d_{x^2-y^2}$ orbital, as expected, but a significant mixing with the $3d_{z^2}$ orbital is also observed. Model DV-X_α calculations support these conclusions. A contraction of the copper 3d spin density in real space is observed, which is at least partly due to spin polarization, an electron–electron correlation effect.

1. Introduction

We are currently investigating the spin and charge densities in $M(H_2O)_6^{2+}$ ions in ammonium Tutton salts, $(NH_4)_2M(II)(SO_4)_2 \cdot 6H_2O$, by means of polarized neutron diffraction (PND) and x-ray diffraction experiments. To throw more light on the covalence in the bonding in the Cr(II) and Cu(II) cases, which are Jahn–Teller distorted, we have analysed the PND data of Menzinger *et al* [1] on anhydrous cupric sulphate, $CuSO_4$, and report the results here.

The crystal structure of $CuSO_4$ has been investigated by x-ray [2, 3] and neutron diffraction [1] methods. The crystal is orthorhombic, *Pbnm*, with the copper(II) ions at four sites of inversion symmetry. Each copper site is octahedrally coordinated by six sulphate oxygen atoms, of three independent types. The bond lengths are markedly Jahn–Teller distorted: Cu–O(1), 2.37 Å; Cu–O(2), 2.03 Å; Cu–O(3), 1.89 Å. O(1) and O(2) coordinate two copper ions separated by the distance $c/2$. O(3) coordinates only one copper atom. O(1), O(2) and the S atom all lie on a plane of mirror symmetry, defined by $z = 0.25$ and c.

Below 35 K the crystal is antiferromagnetic [4–9]. Powder neutron data [10] and the PND data define the magnetic structure unambiguously from the pattern of absences in the magnetic structure factors and the large and small intensity classes of reflection. In the $(0kl)$ and (hhl) zones $(0k0)$ and $(hh0)$ are all absent while $(0kl)$, k odd, and $(00l)$, l even, are also zero within a few thousandths of a Bohr magneton (μ_B) per Cu^{2+} ion. Of the remaining reflections, those with l even have small but non-zero (less than about $0.05~\mu_B$) magnetic structure factors, while those with l odd have large values which, for the $(0kl)$ zone experiment, very roughly follow a Cu^{2+} magnetic form factor.

The magnetic structure deduced from the above information consists of all moments throughout the cell collinear with and parallel to a, with positive moments in the $(0,0,0)$ and $(\frac{1}{2},\frac{1}{2},0)$ coordination region and negative moments for the $(0,0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ regions.

Menzinger *et al* made no attempt to fit the data further in a quantitative manner but noted that the large deviation of the 'allowed' l-odd reflections from a smooth curve and the non-zero values for the l-even 'allowed' reflections imply a very anisotropic distribution of the magnetization on the copper site. Fourier maps showed such a feature and also indicated the presence of magnetization density away from the copper sites, i.e. covalence in the copper–oxygen bonds.

In similar situations, e.g. $CuCl_2 \cdot 2D_2O$ [11], $Cr(OD_2)_6^{2+}$ [12], and many other transition-metal complexes [13] we have been able to fit by least-squares methods a simple model for the magnetization density which reveals covalence in the metal–ligand bonding and anisotropy in the magnetization at the metal atom site. We reanalyse the data of Menzinger *et al* in that way below.

2. Least-squares analysis of magnetic data

We have found elsewhere [14] that reflections of low nuclear structure factor are very susceptible to systematic error, often from multiple-scattering effects. We have removed all reflections of nuclear structure factor less than 10^{-14} m from the data of Menzinger *et al* to give the set with which we deal. After we further removed those reflections which are identically zero in the above collinear model, only 53 unique reflections remained. Consequently, our choice of model to refine cannot be as flexible as in other cases, e.g. $CoCl_4^{2-}$ [14].

On the copper site we refined populations in $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals, and a $3d_{z^2}/3d_{x^2-y^2}$ mixing function. We also refined a parameter which defines 3d radial extent. A dipole correction [15] for the scattering by the orbital moment with $g = 2.43$, derived from the single-crystal magnetic susceptibility data [7, 8], was used. Within this approximation our refined populations are in spin units. O(1), O(2) and S occupy a mirror plane of magnetic antisymmetry and so can have no net spin population. We refined a (10) dipolar multipole oriented along c, with 2p (3p for S) radial dependence on each such atom. On O(3) we refined a spherical population with 2p radial dependence. In addition, we refined the population of a Gaussian function of RMS width 0.4 Å at each Cu–O bond midpoint. The $(0kl)$ data are on an absolute scale, but the (hhl) data, for experimental reasons, are not; so we refine a scale factor for the (hhl) data. The resulting 12-parameter model was refined to give a fit of $R(F) = 0.129$, $R_w(F) = 0.083$ and $\chi^2 = 2.20$. The results are listed in table 1. Table 2 shows a list of observed and calculated structure factors. The large and significant differences between observed and calculated results are concentrated on those reflections of low nuclear structure factor $((041), (005), (067), (113), (331)$ and $(444))$ with only the high F_N for (025) as an exception. Use of a scale factor to modify the observed magnetic structure factors in the (hhl) zone is only correct in the limiting case where, in the observed flipping rates, we can neglect the terms in $(F_M/F_N)^2$ compared with those in F_M/F_N. Subsequent calculations on the two reflections remaining with F_M/F_N over 0.25 show that, while not negligible, the effect is small. The largest correction is for (113) where $F_M(\text{obs})$ should be reduced by 1.15 rather than the 1.10 of the linear approximation. In both (113) and (331) the use of the correct rather than approximate formula improves the agreement between observed and calculated; for example, for (113), $F(\text{obs}) - F(\text{calc})$ decreases from 0.15×10^{-14} to

Table 1. Population and other parameters from magnetic refinements of PND data for $CuSO_4$ (units of population, spins).

Cu	
3d populations	
$3d_{x^2-y^2}$	0.48(10)
$3d_{z^2}$	0.28(9)
$3d_{z^2}/d_{x^2-y^2}$ mixing	−0.34(16)
Total 3d population	0.77(5)
3d radius (X free Cu^{2+})	0.86(6)
Cu–O(1) overlap, monopole	−0.02(2)
Cu–O(2) overlap, monopole	0.02(2)
Cu–O(3) overlap, monopole	0.04(5)
O(1) population, dipole (10)	−0.01(1)
O(2) population, dipole (10)	0.00(1)
O(3) population, monopole (00)	0.04(2)
S population, dipole (10)	0.03(2)

0.12×10^{-14} m/unit cell. The refined scale factor causes the published magnetic structure factors for (hhl) to be overestimated by a factor of 1.10(6).

The improvement in the fit over the model involving only a refinable spherical copper site population is considerable; then $R(F) = 0.187$, $R_w(F) = 0.164$ and $\chi^2 = 3.90$. Refinement of only a copper site population and the (hhl) scale gave $R(F) = 0.150$, $R_w(F) = 0.114$ and $\chi^2 = 2.80$. A refinement which also included Gaussian functions at sites suggested by the Fourier maps of Menzinger *et al* did not give a significant improvement or significant populations apart from those of the complete refinement. The result was similar when $3d_{xy,xz,yz}$ populations, constrained to be equal, were introduced. When we restricted the 3d population to the $3d_{x^2-y^2}$ orbital alone, the fit was degraded, showing that $3d_{z^2}$ population and its mixing with $d_{x^2-y^2}$ are significant. There resulted $R(F) = 0.123$, $R_w(F) = 0.093$ and $\chi^2 = 2.42$, with a $3d_{x^2-y^2}$ population of 0.72(5) spin.

3. X_α calculations

The discrete variational X_α (DV-X_α) scheme has been described elsewhere in detail [16–20]. It employs numerical basis functions in the solution of an unconstrained Hartree–Fock–Slater local-density formalism. Our calculations proceeded as before [11] for the various copper clusters calculated for $CuCl_2 \cdot 2D_2O$. A calculation on a $Cu(SO_4)_6^{10-}$ cluster was too complex for our local computing facilities. As approximations to that we have calculated for $Cu(O)_6^{10-}$ and $Cu(OH_2)_6^{2+}$ units, each with mmm symmetry and with the experimental Cu–O bond lengths in $CuSO_4$.

For the $Cu(O)_6^{10-}$ cluster we find a Cu population of 0.892, an O(1) population of −0.001, O(2) population of 0.023, and O(3) of 0.031 spin. For the $Cu(OH_2)_6^{2+}$ cluster, we found a Cu population of 0.903, water (O(1)) population of −0.001, water (O(2)) population of 0.021 and O(3) of 0.029 spin. The copper configuration in both cases shows almost all spin in the $3d_{x^2-y^2}$ orbital, but with substantial mixing with $3d_{z^2}$ (parameters, −0.18 and −0.20).

Table 2. Comparison of observed magnetic structure factors [1] and those calculated from our least-squares model. Note that we have retained the values of Menzinger *et al* values for the (hhl) zone and increased the calculated values by 1.10 so as to maintain easy comparability with their tables, rather than reducing the observed values by 1.10(6) as our modelling indicates. Values of the nuclear structure factor are also given. The list for each zone is in increasing $(\sin\theta)/\lambda$.

h	k	l	F_M(obs) $(10^{-14}$ m/unit cell)	F_M(calc) $(10^{-14}$ m/unit cell)	$\sigma(F_M$(obs)) $(10^{-14}$ m/unit cell)	F_N $(10^{-14}$ m/unit cell)
0	0	1	0.995	0.993	0.007	0
0	2	1	0.763	0.800	0.049	−2.726
0	2	2	−0.001	−0.002	0.003	4.171
0	0	3	0.690	0.655	0.030	0
0	4	1	0.726	0.591	0.027	1.375
0	2	3	0.571	0.632	0.039	−3.378
0	4	2	0.060	0.068	0.009	4.563
0	2	4	−0.008	−0.007	0.008	1.926
0	6	1	0.409	0.430	0.024	1.059
0	0	5	0.500	0.390	0.080	0
0	6	2	0.408	0.057	0.010	1.585
0	2	5	0.304	0.369	0.011	−4.823
0	6	3	0.376	0.362	0.021	4.764
0	4	5	0.336	0.332	0.011	1.549
0	2	6	0.026	−0.004	0.015	4.348
0	6	4	0.069	0.063	0.015	4.933
0	8	2	0.053	0.048	0.012	2.923
0	4	6	0.042	0.008	0.031	10.624
0	6	5	0.295	0.262	0.010	3.175
0	0	7	0.240	0.187	0.120	0
0	8	4	0.051	0.058	0.020	5.625
0	6	7	0.216	0.163	0.013	1.699
0	10	3	0.117	0.143	0.014	−4.501
0	4	8	−0.016	−0.012	0.009	2.901
0	2	9	0.084	0.074	0.018	1.309
0	10	5	0.143	0.128	0.009	−2.813
0	0	1	0.964	0.993	0.050	0
1	1	1	0.753	0.797	0.025	3.231
1	1	2	0.058	0.057	0.011	1.569
2	2	1	0.602	0.634	0.025	4.429
1	1	3	0.840	0.673	0.036	−1.654
2	2	2	0.051	0.046	0.006	3.899
1	1	4	0.020	0.000	0.015	3.976
3	3	1	0.585	0.512	0.035	−1.093
2	2	4	0.077	0.052	0.010	2.424
3	3	2	0.037	0.040	0.006	1.330
1	1	5	0.337	0.401	0.026	3.623
3	3	3	0.375	0.406	0.026	−2.224
2	2	5	0.286	0.334	0.036	5.950
1	1	6	−0.036	0.005	0.015	3.027
3	3	4	0.078	0.049	0.029	2.904
4	4	2	0.027	0.050	0.022	4.518
2	2	6	0.024	0.016	0.004	3.436
3	3	5	0.238	0.264	0.026	−2.246
1	1	7	0.231	0.198	0.023	−2.197
4	4	4	0.050	0.068	0.005	1.029

Table 2 *continued*

h	k	l	F_M(obs) (10^{-14} m/unit cell)	F_M(calc) (10^{-14} m/unit cell)	$\sigma(F_M$(obs)) (10^{-14} m/unit cell)	F_N (10^{-14} m/unit cell)
3	3	6	−0.016	0.034	0.038	5.452
2	2	7	0.184	0.169	0.020	−1.976
5	5	1	0.189	0.252	0.027	−1.367
1	1	8	−0.028	−0.004	0.051	4.678
5	5	2	0.074	0.049	0.035	3.893
5	5	3	0.150	0.205	0.031	−3.064
2	2	8	−0.012	−0.001	0.006	2.171
4	4	6	0.059	0.053	0.012	5.333

4. Discussion

4.1. DV-X$_\alpha$ results

We discuss the DV-X$_\alpha$ calculation results first, since our purpose in performing them was to provide justification for the model used in the interpretation of the experimental data. Because of the limited basis employed and the cluster approximations, we only use the results qualitatively.

The wavefunctions of both clusters show just the relative features expected from the bond lengths and are remarkably similar. Covalence, measured by the coefficients in the wavefunctions, is marked, with spin transfer increasing as the Cu–O bond lengths decrease from Cu–O(1) to Cu–O(3). The copper site spin configuration is dominated by population of the 3d$_{x^2-y^2}$ orbital, with z taken along the long Cu–O(1) bond. There is significant mixing with 3d$_{z^2}$, which has the same a$_{1g}$ symmetry in mmm. The spin–hole molecular orbital in both cases has coefficients 0.96 for the 3d$_{x^2-y^2}$ and −0.1 for the 3d$_{z^2}$ orbital. The mixing coefficient between these orbitals is negative, indicating a rhombic distortion of spin density caused by the higher covalence of the Cu–O(3) than the Cu–O(2) bonding. The net influence on the spin density is an expectation that covalent spin transfer of about 0.1 spin to oxygen atoms should be observed, the more so across the shorter bonds. The copper configuration should be dominated by the 3d$_{x^2-y^2}$ orbital population, but we may observe 3d$_{z^2}$–3d$_{x^2-y^2}$ mixing, even though the 3d$_{z^2}$ orbital population itself may be negligible.

4.2. PND analysis

Given the above DV-X$_\alpha$ results, in spite of the low local symmetry, we may expect a rather simple model invoking only σ donation and 3d$_{z^2}$–3d$_{x^2-y^2}$ mixing to provide a relatively good account of the spin density. In this antiferromagnetic system there is one further complication. Any spin density delocalized onto O(1), O(2) and S from the copper site at (0, 0, 0) will be at least partly cancelled by the spin of the opposite sign delocalized from the copper atom at (0, 0, $\frac{1}{2}$), where the spin is of opposite spin.

In table 1 we see that only 0.77(5) spin remains on the copper site, and 0.23(5) has been delocalized onto the sulphate groups by covalent interactions. 0.08(5) spin appears in each Cu–O(3) bond, equally divided between the oxygen and the midbond regions.

The total spin observed, 0.93(5) units, is marginally reduced below unity, indicating some smaller covalence in the Cu–O(1) and Cu–O(2) bonding. Examination of the midbond populations suggests that covalence in the Cu–O(1) bonding is negligible, since the population is not significantly positive. Further evidence is contained in the dipolar populations. We do not expect complete antiferromagnetic cancellation of spin if the spin distributions on the oxygen sites are not spherical. For O(1) and O(2) the dipole population is not significant. For S, however, we have 0.033(17) spins in each dipole lobe, with positive spin in the lobe pointing along $-z$, i.e. positive spin linking with the positive spin on O(3).

While none of the covalent spin transfers mentioned above is significant at better than the 2σ level, together these results consistently indicate that Cu–O(3) spin transfers dominate the covalence in the Cu–O bonding, with the other two interactions less important. We also see a spin-coupling pathway Cu–O(3)–S–O(3)–Cu, by which the antiferromagnetic ordering could be accomplished.

On the copper site, while the $3d_{x^2-y^2}$ orbital population dominates, the $3d_{z^2}$ population and the $3d_{z^2}$–$3d_{x^2-y^2}$ mixing are both significant. Both these features can, in a first approximation at any rate, be accommodated by a spin-hole wavefunction of the form

$$\psi = 0.79|3d_{x^2-y^2}\rangle - 0.36|3d_{z^2}\rangle + 0.50 \text{ (ligand contributions)}.$$

However, given the uncertainty in the correction for orbital magnetization and our neglect of configuration interaction and relativistic spin–orbit coupling effects, the only certain conclusion is that some contribution from $3d_{z^2}$ appears in the ground state, and that may involve something more complicated than a simple spin-hole molecular orbital.

The copper-centred radial spin distribution appears to be contracted 14(6)% from a restricted Hartree–Fock calculation of the Cu^{2+} form factor [21]. There are uncertainties in the orbital moment correction, and the effects of the covalency on the 3d copper functions are not known. However, it is known that electron–electron correlation effects in the free ion contract a theoretical unconstrained Hartree–Fock wavefunction, and the change is even more apparent in the presence of an octahedral crystal field. The Ni^{2+} ion in NiO is 6% compressed relative to an RHF calculation [22]. The contraction in Cu(II) case observed here and in other studies is at least partly due to correlation effects. The correlation effects may also be described as spin polarization.

Acknowledgment

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