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SPIN DENSITY IN A BIMETALLIC MAGNETIC CHAIN $MnCu(pba)(H_2O)_3.2H_2O$: A POLARISED NEUTRON DIFFRACTION STUDY

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Abstract The compound $MnCu(pba)(H_2O)_3.2H_2O$ (**1**), with pba = 1,3-propylenebis(oxamato), in which the Mn^{2+} and Cu^{2+} ions, linked together by oxamato bridges, form chains running along the crystallographic b direction, shows the magnetic behaviour characteristic of one dimensional ferrimagnet. A polarised neutron diffraction experiment on a single crystal of (**1**) has been performed in order to determine the spin distribution along the magnetic chain. The magnetisation density, induced by a magnetic field of 5 Teslas, has been obtained at 10 K. The strong positive spin population for Mn and the negative one for Cu confirm the antiferromagnetic nature of the intrachain coupling. The oxygen and nitrogen atoms of the oxamato group carry small spin populations, with the same sign as the metallic ion to which they are linked. A striking result is the negative spin density found on the two central carbon atoms, which can be interpreted by spin polarization effects.

INTRODUCTION

The compound $MnCu(pba)(H_2O)_3.2H_2O$ (**1**), with pba = 1,3 propylenebis(oxamato) may be considered as the archetype of ferrimagnetic bimetallic chains[1]. The $\chi_M T$ versus T plot shows the characteristic behavior of this new class of compounds with a minimum at T = 115 K. As the temperature is cooled further below that temperature, $\chi_M T$ increases more and more rapidly, in a ferromagnetic fashion, before showing a sharp maximum at 2.2 K due to the onset of a three-dimensional antiferromagnetic ordering of the ferrimagnetic chains. The intrachain interaction parameter between nearest neighbor

Mn^{2+} and Cu^{2+} ions is found as J = - 23.4(4) cm^{-1}, the interaction Hamiltonian being of the form $\mathbf{H} = - J\ S_i\ \underline{S}_{Mn,i} \cdot \underline{S}_{Cu,i}$. This large value, in spite of a Mn...Cu separation of 5.412 Å, is due to the conjugated nature of the oxamato bridge. A thorough understandig of the mechanism of the interaction requires to know to what extent the spin densities arising from the metal ions are delocalized toward the bridging atoms. This paper is devoted to this problem.

EXPERIMENTAL

Synthesis

A blue single crystal of (**1**) was obtained by slow diffusion of isoconcentrated aqueous solutions (c = 0.09 $mol.l^{-1}$) of $Na_2(Cu(pba)).6H_2O$, synthesized according to the previously reported procedure[2], and $Mn(ClO_4)_2.6H_2O$, in a H-shaped tube within about six months at 50°C. The crystal had the shape of a plaquette of dimensions 0.5 x 4 x 7 mm, with the long dimension along <u>c</u> and the <u>a</u> axis perpendicular to the plaquette. It has been used for both structural and spin density investigations.

Crystallographic Structure

The crystallographic structure of (**1**) was known from X-ray diffraction at room temperature[1]. In order to determine the atomic positions and thermal parameters at low temperature, including those of the hydrogen atoms, we performed an unpolarized neutron diffraction experiment at 10 K, on the four-circle diffractometer DN4 of the MDN Laboratory, at Grenoble's SILOE Reactor. $MnCu(pba)(H_2O)_3.2H_2O$ crystallizes in the centrosymmetric space group Pnma, with Z = 4, and a = 12.734 Å (12.945 Å), b = 21.352 Å (21.250 Å), c = 5.154 Å (5.210 Å), where the values in parentheses correspond to the parameters at 294 K. No phase transition was observed down to 10 K. The a and c cell parameters are slightly shortened at low temperature, while a small lengthening of b is observed.

The structure consists of chains of Mn and Cu, separated by an

oxamato bridge, which are parallel to the b axis. The structure of the chain motif at 10 K is shown in Figure 1. The Mn^{2+} ion, located at a centrosymmetric center, is surrounded by an octahedron of six oxygen atoms. The apical oxygens (O4) originate from two water molecules, while the oxygens of the equatorial plane (O1,O2) belong to two organic bridges. At low temperature, the three Mn-O bond lengths are very close to each other: Mn-O4 = 2.177 Å, Mn-O1 = 2.168 Å and Mn-O2 = 2.181 Å. The copper environment is an approximate square pyramide formed by the oxygen from a water molecule (O5) and the oxygen and nitrogen atoms from two oxamato bridges (O3,N1), with a crystallographic mirror plane passing through the Cu and O5 atoms. The distance between Cu and the apical oxygen Cu-O5 = 2.266 Å is significantly larger than the bond lengths of the basal plane: Cu-O3 = 1.991 Å and Cu-N1 = 1.943 Å. The oxamato group and the Mn and Cu basal planes are practically coplanar. The carbon-oxygen (C2-O1 = 1.290 Å, C1-O2 = 1.251 Å, C1-O3 = 1.276 Å) and carbon-nitrogen (C2-N1 = 1.297 Å) bond lengths are closer to partially double than to simple bonds, whereas the carbon-carbon bond (C1-C2 = 1.525 Å) has essentially a simple bond character.

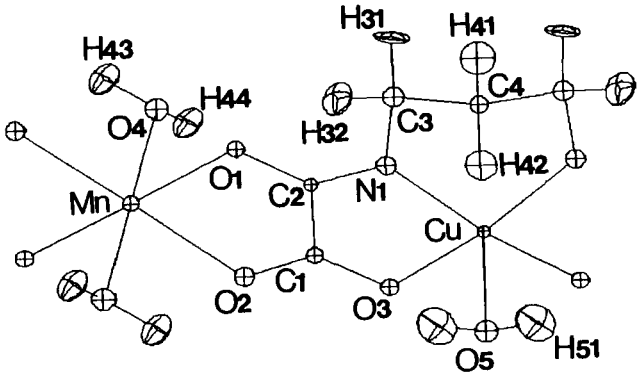

FIGURE 1 Structure of (1) at 10K in projection along c.

As a general remark, all bond lengths along the chain increase from 294 K to 10 K, while the distances along the a or c axis

decrease. As a result, the chains draw nearer to each other, but become more elongated along the chain direction, as shown by the increase of the shortest Mn...Cu distance within the chain from 5.412 Å to 5.431 Å, and the decrease of the shortest separation between metal atoms belonging to neighboring chains Cu...Cu = Mn...Mn from 5.211 Å to 5.154 Å.

Magnetic properties

The magnetic properties of (**1**) have been investigated by magnetic susceptibility measurements on powder[1] and single crystal[3]. The minimum of the $\chi.T$ curve at 115 K is well interpreted by a model of antiferromagnetically coupled chains of Mn^{2+} (S=5/2) and Cu^{2+} (S=1/2) spins. The magnetisation M at 10 K has been measured as a function of the magnetic field on a polycrystalline sample. M is found equal to 3.5(2) μ_B/mol for a field of 5 Teslas.

Magnetic anisotropy has been observed on a single crystal[3] below 5 K, the easy magnetisation axis being along c down to 2.5 K. A maximum at 2.2 K in the $\chi(T)$ curve corresponds to the antiferromagnetic ordering between the chains. The magnetic susceptibility measured on a single crystal reveals the existence of a weak ferromagnetic component along a in the AF ordered phase[3].

Polarized Neutron Diffraction

The physical phenomenon which is involved in polarised neutron diffraction is the magnetic interaction between the incident neutron spin and the magnetic moments inside the material. A magnetic field parallel to the polarization direction of the incident neutrons is applied to the sample in order to align the electronic spins. The intensity diffracted by a single crystal for the incident neutron beam with spin up or spin down respectively is a function of the magnetic and nuclear structure factors F_M and F_N of the Bragg reflection (hkl):

$$I_{\pm}\ (hkl)\ \alpha\ |F_N \pm F_M|^2$$

where the sign of F_M depends on the incident neutron polarisation.

The ratio between the intensities I_+ and I_- at the Bragg peak position, so-called flipping ratio, is actually measured:

$$R(hkl) = \frac{I_+(hkl)}{I_-(hkl)} = \frac{(F_N + F_M)^2}{(F_N - F_M)^2} \qquad (1)$$

This expression is valid if the crystal has a centrosymmetrical structure[4]. The F_M/F_N ratio is overtaken by solving a quadratic equation derived from relation (1). Generally only one of the two solutions has a physical meaning. The magnetic structure factors can then be determined, if the nuclear structure factors are known. The preliminary determination of the nuclear structure in the same conditions of temperature as the polarised neutron experiment is necessary to obtain accurate F_N values.

The experiment was performed on the normal beam-polarized neutron diffractometer 5C1 of L.L.B. at Saclay's ORPHEE Reactor. A monochromator polarizes the incident neutron beam and selects the wavelength (0.83 Å). The neutron beam polarization was equal to 0.92. A flipper device changes alternately the sign of the polarization of the neutron beam along the vertical direction. The experimental conditions of temperature and field applied to the sample were obtained with help of a superconducting cryomagnet. The crystal was cooled down at 10 K and submitted to a high magnetic field, H = 5 T, permitting to reach 89 % of the magnetic saturation. Two data collections were performed, for the crystal being set with the c axis vertical and then with b vertical. Two sets, consisting of 209 (with l = 0 to 2) and 89 (with k = 0 to 7) (hkl) independent reflections respectively, were collected within $\sin\theta/\lambda = 0.5$ Å^{-1}. Due to a difficulty belonging to the flipping ratio technique in the case of extreme R values, only reflections with $0.5<R(hkl)<2.5$ have been kept.

RESULTS

Fourier summation

The magnetisation density can in principle be obtained by a Fourier summation of the magnetic structure factors:

$$\rho(\underline{r}) = \Sigma_{hkl} F_M(hkl) e^{2\pi i(hx+ky+lz)}.$$

However the series should be infinite, or at least complete up to large values of h, k, l indices in order to get a non-biased image of the spin density. This is not the case for the present study for which about 70 per cent of the magnetic structure factors are lacking within $\sin\theta/\lambda = 0.5$ Å^{-1}. These components could not be measured by polarised neutron diffraction because the corresponding nuclear structure factors were also too small to provide a peak with large enough intensity to be discriminated from the background.

The Fourier map in Figure 2 represents the projection of the spin density along $\underline{c}$ obtained by Fourier summation of 78 magnetic structure factors $F_M(hk0)$, including the $F_M(000)$ contribution. The value of $F_M(000)$ corresponds to the total magnetisation in the cell and was taken equal to 14 μ_B according to the magnetisation measurements. A strong positive spin density centered on the manganese atom is observed, while a region of negative spin density around the copper atom can be noticed. The contours which can be seen out of any atomic positions are due to the incompletness of the Fourier series.

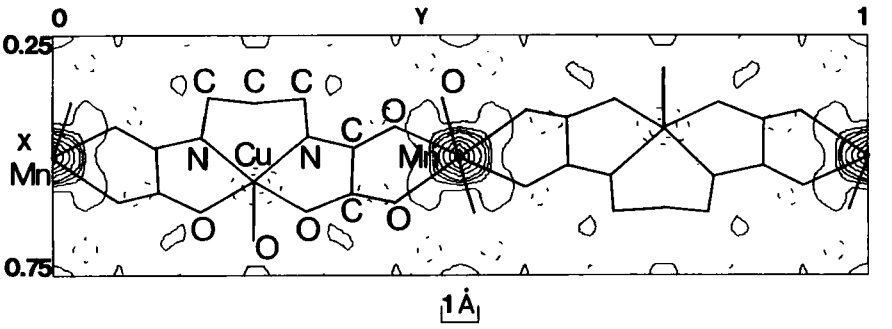

FIGURE 2 Induced spin density map at 10K under 5 Teslas, projected along $\underline{c}$, obtained by Fourier summation. The levels are going from 0.25 to 1.0 $\mu_B/Å^2$ with intervals of 0.25 $\mu_B/Å^2$ and from 1.0 to 3.0 $\mu_B/Å^2$ with intervals of 0.5$\mu_B/Å^2$. The dashed lines are the corresponding negative levels.

Model refinement

In order to extract more detailed informations on the magnetisation density $\rho(\underline{r})$ from the magnetic structure factors, we have to define a model for $\rho(\underline{r})$ and refine the parameters of this model on the observations. The following assumptions are taken into account for the model definition:

- the magnetisation density is the sum of densities $\rho_i(\underline{r}_i)$ centered on the atoms in the cell, where $\underline{r}_i$ are local atomic coordinates:

$$\rho(\underline{r}) = \Sigma_i \rho_i(\underline{r}_i)$$

- the magnetic electrons responsible for the magnetisation are located in molecular orbitals which are linear combinations of 3d orbitals on Mn, Cu and 2p orbitals on N, C, O. Each atomic orbital can be written as the product of a Slater type radial function by a real spherical harmonics:

$$\phi_{3d}(\underline{r}_i) = N\, r_i^2\, e^{-\xi r_i}\, y_{lm}(\theta_i,\phi_i) \qquad (2)$$

$$\phi_{2p}(\underline{r}_i) = N\, r_i\, e^{-\xi r_i}\, y_{lm}(\theta_i,\phi_i)$$

where ξ is a Slater exponent and y_{lm} a combination of spherical harmonics Y_{lm}. The theoretical spin density expressed from the molecular wavefunction is a linear combination of 3d3d, 2p2p and 3d2p products of atomic orbitals. The product of two Slater functions is also of Slater-type and the product of two spherical harmonics is a spherical harmonics. This is the reason why a set of functions build up as products of a Slater radial function and a spherical harmonics forms a well adapted basis set for the analytical description of the spin density[5]. These functions $\rho_{lm}(\underline{r}_i)$ are called multipole functions:

$$\rho(\underline{r}_i) = \Sigma_l \Sigma_m P_{lm}\, \rho_{lm}(\underline{r}_i)$$

with

$$\rho_{lm}(\underline{r}_i) = N_{lm}\, r_i^{n_l}\, e^{-K\zeta r_i}\, y_{lm}(\theta_i,\phi_i) \qquad (3)$$

The parameters to be refined are the coefficient K of the Slater exponent ζ and the multipole populations P_{lm}. By analogy between

relations (2) and (3), the Slater exponents ζ are chosen to be equal to 2ξ, where ξ has the value of the exponent optimised for atomic wavefunctions : ζ = 7.02, 8.8, 3.9, 3.44 and 4.50 au^{-1} for Mn, Cu, N, C and O respectively[6]. The coefficient n_0 is taken equal to 4 for the 3d ions Mn and Cu, and to 2 for the 2p atoms N, C and O. The multipole development has been restricted to the spherical terms l = 0, for all the atoms. Only the atoms belonging to the bridge and the atoms directly bonded to the metal ions have been taken into account. A coefficient K has been refined for the Mn atom, in order to in a more satisfying fashion represent the radial expansion of the spin density distribution around Mn. Only reflections with $|F_M| > 2\sigma$ were used. The refinement was carried out on a total of 202 independent observations: the two separate data collections yield respectively two sets of 169 and 64 experimental magnetic structure factors, including 31 common reflections. A scale factor has been refined for the second set with respect to the first one and a value of 0.88(1) was obtained. A goodness of fit χ^2 of 4.8 and a weighted agreement factor of 0.081 were obtained.

The integration of the magnetisation density $\rho(\underline{r})$ over the unit cell gives simply the sum of the monopole populations P_{00}, which is then equal to the magnetisation in the cell. The normalisation of the refined monopole populations to a total spin of 4 yields the values of the spin populations reported in Table I. The projection of the spin density perpendicularly to the O2-Mn-O1 plane is drawn in the Figure 3.

The antiferromagnetic coupling between Mn and Cu is confirmed by the value of the strongly positive spin population of 4.95 on Mn and the negative one of -0.76 on Cu. On the bridge, weak positive population of 0.02 are observed on the oxygen O1 and O2 linked to the manganese ion, while weak negative populations are seen on the nitrogen and oxygen atoms N1 (-0.06(2)) and O3 (-0.05(2)) linked to the nitrogen. The same respective signs are found for the oxygens which are not involved in the bridge, O4 (0.04(2)) linked to Mn and O5

(-0.03(3)) linked to Cu. The presence of significant negative spin density on the central carbons C1 and C2, with populations of -0.05(2) and -0.07(2), is quite remarquable.

TABLE I Spin populations p, obtained by multipole refinement.

atom	p
Mn	4.95(5)
Cu	-0.76(3)
O1	0.022(17)
O2	0.024(17)
O3	-0.052(18)
O4	0.037(18)
O5	-0.031(28)
N1	-0.062(23)
C1	-0.053(23)
C2	-0.071(22)

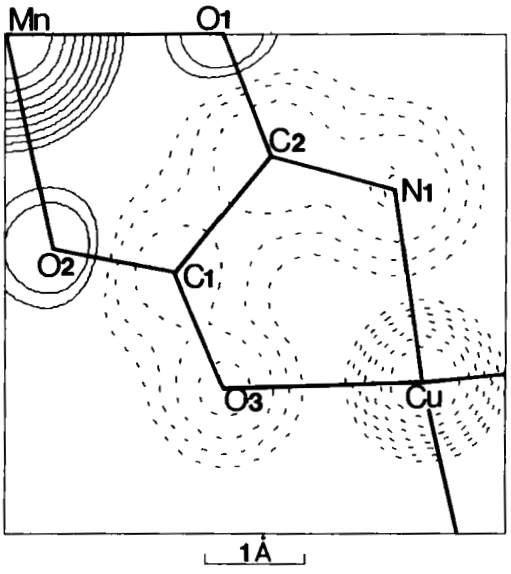

FIGURE 3 Projection of the induced spin density, obtained by multipole refinement, perpendicularly to the oxamato bridge. The contours are defined by $\pm 0.005\ 2^{n-1}\ \mu_B/Å^2$, where n is the number of the outline. Negative levels are dashed.

DISCUSSION AND CONCLUSION

The first information arising from this investigation concerns the antiferromagnetic nature of the interaction. The spin densities on the Mn and Cu atoms are positive and negative, respectively. The ratio between the Mn and Cu spin populations is equal to - 6.5. This ratio would be equal to - 6.97 for the S = 2 ground state of a $Mn^{2+}Cu^{2+}$ pair without spin delocalization, and roughly to - 5 for a classical chain with an alternation of the local spins. The spin densities on the bridging atoms first reveals the spin delocalization. The oxygen atoms bound to Mn have a weak positive spin density, and the nitrogen and oxygen atoms bound to copper a weak negative spin density. More surprising is the presence of a significant negative spin density on the carbon atoms of the oxamato bridge. It is too early to interpret this result. We may say, however, that the mechanism of the interaction is more complex than what had been suggested so far. Probably, not only spin delocalization and overlaps of magnetic orbitals play a role, but also spin polarization effects. We hope to be able soon to rationalize those findings, and to get new insights on the mechanism of the magnetic interaction through extended bridges.

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