

Spin-dependent covalence in $\text{La}_2\text{CuO}_{4-\delta}$ from neutron diffraction

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We have analyzed the existing magnetic neutron diffraction data on the antiferromagnet $\text{La}_2\text{CuO}_{4-\delta}$ using an empirical magnetization-density model. We show that the density is localized in the basal ac plane in the $3d_{x^2-y^2}$ orbital on Cu and along the four short Cu—O(1) bonds. The Cu $3d$ moment is $0.34(2)\mu_B$, and in each Cu—O(1) bond $-0.029(9)\mu_B$. The $3d$ moment is reduced from approximately $1\mu_B$ because the up- and down-spin mainly $3d_{x^2-y^2}$ bands are sufficiently dispersed, because of strong σ covalence, to partially populate the (on average) higher-energy down-spin band. The negative density in the Cu—O(1) bond arises because the down-spin band covalence is much higher than for the up-spin band. This differential covalence has been observed before, e.g., in metal phthalocyanines, and is an electron-electron correlation effect. The Cu—O(1) magnetization density provides a pathway for the strong in-plane magnetic exchange present. The out-of-plane spin density is very small, $-0.002(2)\mu_B$ on O(2), reflecting weak out-of-plane covalence.

INTRODUCTION

We currently have a program for investigating the spin and charge densities in MO_6^{4-} and related species in transition-metal complexes by means of x-ray and polarized neutron diffraction (PND) experiments. To throw more light on the covalence in Jahn-Teller distorted Cr(II) and Cu(II) systems we have reanalyzed existing neutron diffraction data on anhydrous CuSO_4 ,^{1,2} $\text{CuCl}_2 \cdot 2\text{D}_2\text{O}$,^{2,3} CuO ,^{2,4} and K_2CuF_4 .^{2,5} Recently Freltoft *et al.*⁶ published limited unpolarized neutron diffraction data on the antiferromagnetic phase of $\text{La}_2\text{CuO}_{4-\delta}$, but only attempted to account for them using a spherical Cu^{2+} form factor, which gave a poor fit. In addition, Stassis *et al.*⁷ measured the field-induced magnetization in the compound by PND. $\text{La}_2\text{CuO}_{4-\delta}$ is, of course, the precursor crystal of a family of high- T_c superconductors. We here have analyzed the data in terms of a simple empirical model for the magnetization density which we have used for the other Cu(II) systems, to see if there are unusual features in this crystal. In the other systems the magnetization density resembles theoretical calculations in showing substantial covalence and the expected copper electronic configuration, which is a $3d_{x^2-y^2}$ orbital with some mixing of $3d_{z^2}$, where symmetry allows it.

CRYSTAL STRUCTURE

The antiferromagnetic low temperature defective phases of La_2CuO_4 have been investigated by neutron diffraction.^{6,8-12} While the exact defective structures are complex, the analysis of the magnetic form factors requires only the level of accuracy associated with the ideal formula of La_2CuO_4 . This orthorhombic Cmca structure is a slight distortion from an $I4/mmm$ tetragonal unit cell, as in K_2CuF_4 . The copper atom is octahedrally coordinated by oxygen atoms, with a substantial Jahn-

Teller distortion involving two long Cu—O bonds of 2.39 Å along b and four shorter such bonds of 1.90 Å in the ac plane. We use the orthorhombic cell throughout. The Cu atoms occupy $0,0,0$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$; and $\frac{1}{2}, 0, \frac{1}{2}$; while, in Cmca, O(1), O(2), and La occupy more general positions. Since the orthorhombic distortion is small, we assume O(1) occupies $\frac{1}{4}, 0, \frac{1}{4}$ and O(2), $0, 0.1824, 0$, which are their positions in the superconducting $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-\delta}$.

The diffraction results show that the first two Cu sites described above are magnetized along $+c$, the second two along $-c$. This gives the antiferromagnetic coupling in the ac plane, transmitted through the short Cu—O—Cu bonds. The net moment at each site and the Néel temperature depend on the defect concentration, δ . Kasowski *et al.*¹³ attribute this moment reduction below the expected local moment of $ca\ 1\mu_B$ to the presence of strong covalence. This covalence may also be reflected in the large in-plane Cu—Cu magnetic exchange parameter of $1550(60)$ K.¹⁴ Strong covalence causes highly dispersed bands with eigenvectors composed of combinations of Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals. The dispersion is sufficient to cause the generally lower energy up-band to sometimes exceed the energy of the generally higher energy down-band. Thus both up- and down-bands are populated, the former still dominating, giving a reduction in net spin. Given also the substantial zero-point spin-wave reduction in moment expected for zero-field experiments,¹⁵ the total moment may lie well below the $ca\ 1\mu_B$ expected for a fully ordered $S = \frac{1}{2}$ spin system.

LEAST-SQUARES ANALYSIS OF MAGNETIC DATA

Of the two neutron diffraction experiments, the unpolarized one produces more precise data, so we shall deal with it first. There are only seven reflections measured in this experiment, so the model we use cannot be as flexible as in previous cases, e.g., CoCl_4^{2-} .^{16,17}

We chose to refine a $3d_{x^2-y^2}$ orbital population on Cu

TABLE I. Population and other parameters from refinements of the unpolarized magnetic data (Ref. 6) on $\text{La}_2\text{CuO}_{4-\delta}$. Units of population: μ_B . Parameters marked by an asterisk were not refined.

Refinement	1	2	3	4	5	6	7
Cu $3d$ spherical	0.27(2)	*	*	*	*	*	*
$3d_{x^2-y^2}$	*	0.28(2)	0.27(2)	0.30(1)	0.30(1)	0.34(2)	0.34(2)
$3d$ radius	*	*	0.8(1)	0.93(5)	*	*	*
O(1) sp (dipole)	*	*	*	-0.023(6)	-0.027(6)	-0.010(9)	0.010(9)
O(2) $2p$ (sph)	*	*	*	*	*	*	0.002(2)
Cu-O overlap	*	*	*	*	*	-0.019(9)	-0.019(9)
Total M^a	0.27	0.28	0.27	0.30	0.30	0.26	0.26
$R(F_M)\%$	17.1	12.8	11.1	5.0	6.6	4.6	4.1
$R_W(F_M)\%$	16.5	13.7	10.7	4.4	5.7	4.0	3.4
χ^b	9.6	8.0	6.8	3.6	3.2	2.9	2.8

^aTotal magnetization in unique part of unit cell (μ_B).

^b χ^2 is the goodness-of-fit.

(local axes $z=[010]$, $x=[101]$), and populations on O(1), O(2), and at the Cu—O(1) midbond position. Because of the antiferromagnetic canceling, the monopole O(1) population is zero. We refined the population of a $2s/2p$ sp hybrid orbital, pointing at 0,0,0. This is exactly equivalent to refining a dipole at O(1) with axis [101]. This term thus reflects any incomplete cancellation of spin at O(1). The midbond function of rms half-width 0.4 Å is useful in modeling covalence^{2,16} (and references therein). On O(2) we refined a spherical monopole, with $2p$ radial dependence. We fixed the copper $3d$ radius at its theoretical value and neglected $3d_{x^2-y^2}/3d_{z^2}$ mixing, since the data cannot support more parameters. From our previous refinements we estimate that those would be of lesser significance.

The results of this refinement are given in Table I, and the calculated and observed structure factors in Table II. A four-parameter refinement on seven observables may give values of the parameters which are of limited reliability. We performed a number of other simpler refinements, also in Table I, designed to show the important features of the magnetization density. The largest correlation coefficient in any refinement was -0.89 , and it occurred in the four-parameter refinement.

The eight magnetic structure factors from the PND data have larger relative errors, so we refined only a two-parameter model. The copper $3d_{x^2-y^2}$ population is one parameter and the monopole population on O(1) the oth-

er. We note that for the field induced magnetization the antiferromagnetic cancellation of net O(1) moment no longer applies. We obtained $R(F_M) 0.38R_W(F_M)0.21$ and goodness-of-fit 1.08, with magnetic structure factors given in Table III. The populations obtained are 0.0061(6) on the copper site and $-0.0006(3)\mu_B$ on each O(1) site.

DISCUSSION

From Table I we see that the improvement in fit from the one-parameter spherical $3d$ Cu^{2+} model⁶ to the present four-parameter model is substantial; the R factor falls from 17.1 to 4.1%. Inspection of the intermediate models reveals that this improvement results from two basic causes. Firstly, the localization of the spin in the anisotropic $3d_{x^2-y^2}$ copper orbital, and secondly, and more importantly, the diffuse negative spin density in the ac plane. We obtain a total moment in each unique section of the unit cell of 0.26–0.30 μ_B depending on the model. The moment on the copper site is 0.34(2) μ_B , occupying the $3d_{x^2-y^2}$ orbital as expected.

The diffuse density of $-0.029(9)$ μ_B/Cu , localized along each Cu—O(1) bond, improves the fit considerably, but due to lack of data is not precisely defined in position. This density provides a pathway for the strong magnetic exchange observed.^{14,18} It differs from the other Cu(II) systems we have examined, where the density on the

TABLE II. Observed (Ref. 6) and calculated magnetic structure factors (μ_B per Cu site), for the unpolarized data.

h	k	l	$F_M(\text{obs})$	$F_M(\text{calc})$	$\sigma(F_M(\text{obs}))$
0	0	0	—	0.272	—
1	0	0	0.238	0.242	0.002
0	1	1	0.274	0.246	0.007
0	3	1	0.249	0.252	0.004
0	5	1	0.249	0.233	0.007
3	0	0	0.178	0.178	0.004
3	2	0	0.184	0.180	0.007
5	0	0	0.000	0.001	0.004

TABLE III. Observed (Ref. 7) and calculated magnetic structure factors ($10^3\mu_B$ per Cu site), for the polarized data.

h	k	l	$F_M(\text{obs})$	$F_M(\text{calc})$	$\sigma(F_M(\text{obs}))$
0	0	0	—	4.96	—
0	2	0	5.15	4.89	0.78
0	4	0	4.63	4.78	0.93
2	0	0	5.96	4.93	0.89
2	2	0	3.74	4.81	0.89
0	6	0	3.74	4.50	1.48
0	8	0	4.85	4.15	1.30
4	6	0	4.59	1.11	3.07
0	14	0	-3.33	2.74	4.15

ligand axis is positive. In other M -ligand systems such negative spin density is often seen as a result of the spin polarization of strongly covalent bonds.¹⁹ Qualitatively, such an electron-electron correlation effect can be more usefully discussed within an unconstrained Hartree-Fock framework, as a difference in covalence between up- and down-spin orbitals. In the square-planar coordinated $M(\text{II})$ phthalocyanines, such differential covalence produces dramatic effects in the magnetization density.²⁰ These can be qualitatively explained by noting that the higher energy spin-down $3d$ orbitals are much better matched in energy to the ligand orbitals than are the up-spin orbitals. Accordingly, the down-spin molecular orbitals are predicted to be very much more covalent than up-spin ones,²¹ and in the metal phthalocyanines this is observed to be so.

In the present case, averaged over the highly dispersed occupied bands, the down-spin $3d_{x^2-y^2}$ dominated orbitals are also more covalent than the up-spin orbitals, again because their energy is higher. The difference in covalence appears to be sufficient that even when the larger up-spin component is averaged with the smaller down-spin feature, the down-spin covalent component in the Cu—O bond still dominates. It is interesting that Gillon *et al.* also observe a negative O density in the CuO₂ square-planar net in YBa₂Cu_{2.96(1)}O_{6.41(1)}, although only

at a $1.5\text{-}\sigma$ level of significance.²²

The spin density out of the ac plane, both on the copper site, and along the Cu—O(2) axis, is very small; note the O(2) population of only $0.002(2)\mu_B$. This agrees with the results on CuSO₄ and CuCl₂·2D₂O, where the spin delocalization decreases very rapidly with increase in bond length, as is also expected from theoretical considerations. The PND data adds little to the scene, as its accuracy is low, but it is consistent with this picture. Although induced spin on the O site is of low accuracy, its opposite sign compared to that at Cu resembles the same situation for the small ferromagnetic component of the moment in the canted ferromagnet CuCl₂·2D₂O.

Apart from the complication due to differential covalence, the spin density in La₂CuO_{4- δ} shows no grossly anomalous features as revealed here. Its behavior agrees with theoretical investigations in revealing the importance of strong Cu($3d_\sigma$)—O($2p_\sigma$) in-plane covalent interactions²³⁻²⁷ with little out-of-plane interaction,²³⁻²⁶ thus supporting the popular three-band model of the magnetization.²⁸

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