Extended Moment Formation and Second Neighbor Coupling in Li_2CuO_2

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The Cu-O edge-sharing compound Li_2CuO_2, whose ferromagnetic chains are antialigned, is found from local spin density calculations to display several surprising characteristics: (1) the ordered moment/f.u. of 0.92 μ_B is the largest for any low dimensional cuprate system, in agreement with experiment, (2) 40% of this moment lies on the neighboring O ions, making it equal to the largest oxygen moment yet calculated, and (3) the second neighbor couplings are larger than nearest neighbor couplings. All of these phenomena arise naturally due to an energetically isolated effective d_{yz}-type orbital that includes very strong O p_σ character.

Low dimensional (1D or 2D) spin S=$\frac{1}{2}$ materials display a variety of unusual phenomena in crystals. These range from spin gap behavior in CaV_4O_9 [1] to anomalous spin physics in the one-dimensional spin chains and ladders. [2] Many of these characteristics depend crucially on specific structural or chemical bonding features. [3] The magnetic coupling is particularly sensitive, with simple nearest neighbor (nn) exchange varying from large and antiferromagnetic (AF) to small and ferromagnetic (FM) when the metal-oxygen-metal angle ϕ varies from 180° to 90°. Weak intrachain couplings and competing exchange couplings can lead to frustration, magnetic ordering, spin gap behavior or spin-Peierls phase formation.

Copper oxides play a very important role due to the various possibilities of linking their fundamental unit, a (often slightly distorted) CuO_4 square. Three general types of arrangement can be found in these systems, classified in terms of the oxygen squares sharing corners (as in the high T_c planar compounds and Sr_2CuO_3), edges (as in $CuGeO_3$, $La_6Ca_8Cu_{24}O_{41}$, and Li_2CuO_2), [4], or both (as in $SrCuO_2$). In edge sharing $CuGeO_3$, for example, there is moderately strong AF nn coupling (J≈150 K), [5] but a spin-Peierls transition occurs only at 14 K. The typical example of corner-sharing chains is AF Sr_2CuO_3, [6] with T_N=5 K and a small induced magnetic moment (0.06 μ_B) in spite of very large exchange interactions (J≈2200 K). Despite considerable progress a clear understanding of the magnetic behavior of the Cu^{2+} ion in several regimes is still lacking.

Here we report a new aspect of magnetic polarization in edge-sharing systems revealed by spin-polarized local density approximation (LDA) studies of a 1D S=$\frac{1}{2}$ system Li_2CuO_2. In this compound neutron scattering [7] indicates three dimensional AF ordering at 9 K arising from the antialignment of FM chains. The experimental moment of 0.9 μ_B per cell was attributed completely to the Cu ions. Based upon experience in the undoped two-dimensional cuprates (*viz.* La_2CuO_4) where LDA is unable to obtain any moment whatsoever on the Cu ion [8], it might seem that LDA is unlikely to produce a magnetic Cu ion or an insulating system. Due to this problem in obtaining magnetic Cu ions in Cu-O planes, few spin-polarized calculations on cuprate compounds have been reported. However, we find that LDA predicts Cu in Li_2CuO_2 to be robustly magnetic, allowing us to obtain the relative energies and electronic properties of the system with FM chain with both AF and FM coupling between chains, the AF chain, and the unpolarized (PM) system taken as reference. The oxygen ions play a fundamental role in the band dispersion and the magnetism, and carry a magnetic moment approaching 0.2 μ_B per atom, larger than any reported experimental O moment [9] and equalling the largest calculated O moment.

Li_2CuO_2 is orthorhombic ($a : b : c = 3.654 : 2.860 : 9.377$ $\AA$) and belongs to the category of edge-sharing compounds, with one-dimensional CuO_2 ribbons carrying the Cu chains along the b axis, arrayed in a body-centered fashion in the $a-c$ plane (Fig. 1). The Cu-O-Cu angle $\phi = 94°$ is intermediate between the two other edge-share compounds with very different characteristics: $GeCuO_3$ (spin-Peierls, $\phi = 99°$) and $La_6Ca_8Sr_{24}O_{41}$ (FM, $\phi = 91°$). Distances between two Cu ions, 2.86 Å along the chain, 3.65 Å in the $a-b$ plane and 5.23 Å in the diagonal direction, do not reflect the relative coupling strengths, as we explain below.

Calculations were done using the linearized augmented plane wave (LAPW) method, [10] which makes no shape approximations for the density or potential, and the exchange-correlation potential was that of Ceperley and Alder. [11] The sphere radii used in fixing the LAPW basis were chosen to be 2.00 a.u for Cu and Li and 1.65 for O. Local orbitals (Cu $3p$; Li $1s$; O $2s$) were added to the basis set for extra flexibility and to allow semicore states to be treated within the same energy window as the band states. The plane wave cutoff corresponded to energy of 23.5 Ry resulting in 640 LAPWs per formula unit. Self-consistency was carried out on k-points meshes of 512 points in the Brillouin zone for the compounds which need a single unit cell calculation and 256 points when we considered an

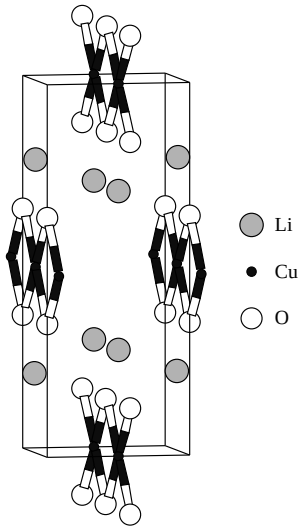

FIG. 1. Crystal structure of Li_2CuO_2, for the AF unit cell containing two CuO_2 ribbons.

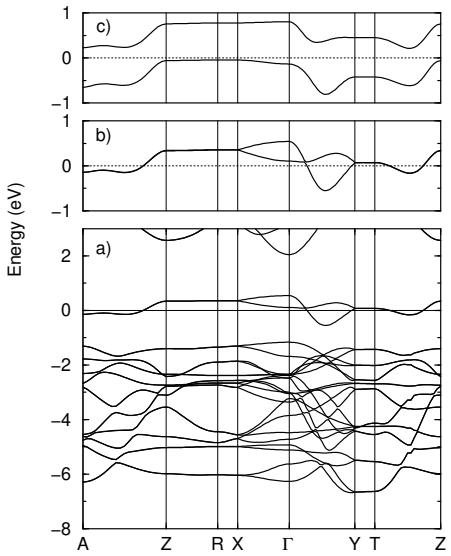

FIG. 2. Band structure of a) paramagnetic Li_2CuO_2, b) a zoom of the region around the Fermi energy, and c) for antiferromagnetic alignment of FM chains. Γ, X, Y and Z points correspond to the standard denomination, $A = (\pi, \pi, \pi)$, $R = (\pi, 0, \pi)$ and $T = (0, \pi, \pi)$; all in the double cell Brillouin zone.

AF arrangement for the chains.

The paramagnetic system has an odd number of electrons per unit cell and thus is metallic. There is a single band in the range of 1 eV around the Fermi level split off from the rest of the $p-d$ band complex, similar to what was found in the other CuO_2 edge-sharing compounds $CuGeO_3$ [12] and $NaCuO_2$. [13]. This isolated band shows up as two bands in Fig. 2, where a doubled cell with two chains has been used for comparison with the AF bands (see below). The analysis of the partial density of states shows that predominantly Cu d_{yz}-O p_σ (the $p_y \pm p_z$ combination directed towards the Cu site) are present in this band.

The geometry of this CuO_2 edge-sharing chain leads to a simple description of the important band, which we expect (and find) to involve an antibonding combination of Cu d and O p orbitals. The atomic orbital basis can be chosen as the Cu d orbitals, the σ-type O p_σ orbitals on each of the *four* neighboring O atoms which strongly overlap the d_{yz} orbital, and half of the out-of-plane p_x orbitals (which are non-bonding). The p_π orbitals in the $y-z$ plane of the ribbon are p_σ with respect to a neighboring Cu and belong to the next unit cell. The d_{yz} and the four p_σ orbitals mix to become five hybridized combinations: one bonding combination $\mathcal{D}_{yz}$ and one antibonding combination $\mathcal{D}^*_{yz}$ of d_{yz} and the linear sum of the four p_σ orbitals with d_{yz} symmetry, and three other p_σ-only combinations of lower symmetry. $\mathcal{D}_{yz}$ and $\mathcal{D}^*_{yz}$ are split strongly, (Fig. 3) leaving $\mathcal{D}^*_{yz}$ at the Fermi level and $\mathcal{D}_{yz}$ 5 eV below. The others lie around -4 eV below E_F and are not of interest. The general behavior of the coupled $d_{yz} - p_\sigma$ cluster can be modelled with $\varepsilon_d = -1.5, \varepsilon_p = -4, (dp\sigma) = \pm 1.15, (pp\sigma) = 0.25$, (all in eV). For these parameters the $\mathcal{D}^*_{xy}$ density is 70% on the Cu and 30% on the four O ions.

The active orbital $\mathcal{D}^*_{yz}$ shown (schematically) as $|\mathcal{D}^*_{yz}|^2$ on next nearest neighbors in Fig. 4, is an effective d_{yz}-type orbital centered on each Cu ion but extending strongly to the neighboring O sites. Symmetry allows direct $\mathcal{D}\mathcal{D}\pi$ overlap, and therefore hopping amplitude t_π along the chain. Due to its parentage, however, it is clear that the main contribution to the overlap arises from the O ion region. If the O quadrilateral were perfectly square ($\phi = 90°$) the O p_σ orbitals directed toward the two neighboring Cu ions would be precisely $p_y \pm p_z$. These combinations are orthogonal, so t_π reduces to direct d-d overlap and will be very small. When the Cu-O-Cu angle is not exactly 90°, the p_σ orbitals are no longer orthogonal and the overlap (and t_π) increases.

The effective Hamiltonian therefore reduces to a single orbital ($\mathcal{D}^*_{yz}$) per cell. The dispersion of the $\mathcal{D}^*_{yz}$ band cannot be fit simply by nn hopping $t_\pi = t_1$ along the chain and t_1' between neighboring chains, but requires as well both next nearest neighbor (nnn) hopping terms t_2 and t_2'. Consideration of the $\mathcal{D}^*_{yz}$ orbitals on second neighbors indicates why this is so: Cu-O-O-Cu coupling along the ribbon becomes important because of O-O coupling and because the nn hopping is so small, and similarly for interchain hopping along the diagonal. The manner of second neighbor overlap along the chain is clear in Fig. 4. The values

$$nn: \quad t_1 = -63\ meV\ , \quad t_1' = -16\ meV,$$
$$nnn: \quad t_2 = -94\ meV\ , \quad t_2' = \ \ 44\ meV,$$

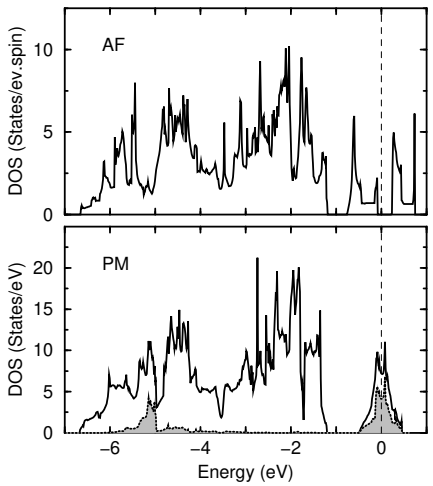

FIG. 3. Density of states for the paramagnetic system and for AF alignment of the chains. In the PM case the partial density of states for the Cu d_{yz} is shown as the shadowed region, illustrating the 5 eV splitting of the $\mathcal{D}_{yz}$ and $\mathcal{D}^*_{yz}$ bands.

(note that second neighbor values are larger than nearest neighbor values), provide an excellent fit to the dispersion over almost the whole zone.

This emergence of an effective single-band system with a simple, strongly hybridized orbital is one of the cleanest in Cu-O systems. It implies that magnetic order in this compound should be interpreted in terms of this extended $\mathcal{D}^*_{yz}$ orbital instead of the Cu d_{yz} orbital; likewise, correlation effects must involve an on-site repulsion $U_{\mathcal{D}}$ rather than U_d and therefore should be smaller than might have been anticipated. Likewise, the exchange splitting of this band will be significantly different from that of the other d orbitals.

The spin wave dispersion curves have been measured by Boehm *et al.* [14] Their fit requires important nnn exchange couplings, consistent with our finding that nnn hopping is essential to account for the dispersion. Although our hopping parameters are small, the exchange constants they obtain are very small, $|J| \leq 0.4$ meV. Application of the superexchange expression $J=4t^2/U$ leads to unphysically large estimates of U≈70-100 eV, indicating that exchange coupling requires more careful consideration.

Relative to the paramagnetic system, the FM state gains 70 meV/f.u. AF chains lead to a slight lowering by another 1.5 meV/f.u., but the phase with oppositely aligned FM chains is lower still (consistent with observation), 80 meV/f.u. below the unpolarized state. The AF gap is 0.32 eV (Fig. 2). As usual, correlation effects will widen the gap, but we are not aware of any published data.

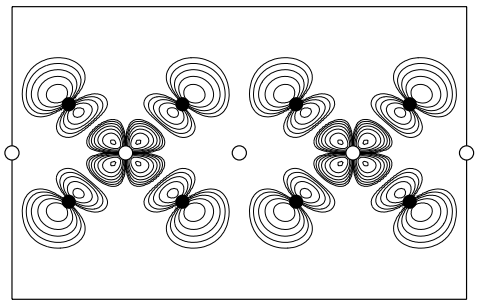

FIG. 4. Illustration of the overlap of two densities $|\mathcal{D}^*_{yz}|^2$ centered on second neighbor Cu ions. Cu and O sites are denoted by empty and filled circles respectively. Model Gaussian d_{yz} and p_σ orbitals were used for this plot.

The moment of 0.92 μ_B per CuO_2 unit is roughly 60% on Cu and 40% on O ions. This transfer of magnetic moment from a transition metal ion to a ligand ion (almost 0.2 μ_B on each O) is equal to the strongest yet reported in a transition metal oxide compound [15] (see below).

To illustrate the importance of the O sites, we display the exchange potential $V_\uparrow - V_\downarrow$ for the FM and AF chains in Fig. 5. There is a clear similarity, especially for the AF chain, to the $\mathcal{D}^*_{yz}$ density in Fig. 4. Two other features should be noted: the exchange potential on O is comparable to that on Cu, and the exchange potential is of predominantly one sign for the entire $\mathcal{D}^*_{yz}$ orbital for both FM and AF ordered chains. Unlike the strong dependence of O moment on the magnetic order, the size of the moment on the Cu ion itself (0.50-0.55 μ_B) is essentially independent of the overall magnetic ordering.

Antialignment of FM chains leads to the insulating band structure shown in Fig. 2(c). As expected, the two bands are described well by the eigenvalues of the system

$$\begin{pmatrix} t_{1,1}(k) + \frac{1}{2}\Delta & t_{1,2}(k) \\ t_{2,1}(k) & t_{2,2}(k) - \frac{1}{2}\Delta \end{pmatrix},$$

where $t_{1,1} = t_{2,2}$ contains all intrachain hopping, $t_{1,2} = t_{2,1}$ contains the interchain hopping given above, and Δ=0.8 eV is the exchange splitting evident in Fig.2(c). Although the chains are nominally fully polarized, the coupling reduces the net moment to $0.92\mu_B$/f.u. This total moment is in excellent agreement with neutron scattering results, [7] although the moment there was

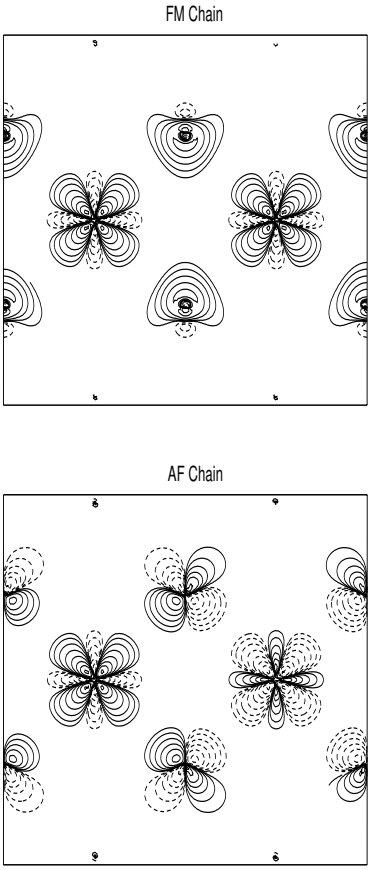

FIG. 5. Exchange potential for ferromagnetic and antiferromagnetic Cu-O chains. Note for the AF case the close resemblance to the $\mathcal{D}^*_{yz}$ orbital density. The solid and dashed lines represent negative and positive values respectively.

attributed solely to Cu. This is a remarkably large value for a quasi-1D S=$\frac{1}{2}$ chain, where quantum fluctuations should be large. The strong nnn coupling that we have uncovered account for the observation qualitatively: coupling between the $\mathcal{D}^*_{yz}$ effective orbitals, and therefore the spins, is really three dimensional, hence quantum fluctuation effects are vastly reduced.

The O moments in Li_2CuO_2 are rivaled in size only by those reported for $SrRuO_3$, [16] Sr_2YRuO_6, [17], and La_2BaCuO_5. [18] Of these, the latter two have isolated CuO_n units (n=6 and 4 respectively), whereas in Li_2CuO_2 the moments are large in spite of overlap of first and second neighbor units. Susceptibility measurements on $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ were interpreted [19] as indicating that each doped hole creates a Zhang-Rice singlet. Our results for Li_2CuO_2 suggest that for edge-sharing chains each extra hole occupies a $\mathcal{D}^*_{yz}$ orbital. In this case the Cu ion and four neighboring p_σ orbitals would simply be non-magnetic, rather than having a Cu spin be compensated by neighboring O spins.

To summarize, we have found that LDA provides a consistent picture of the magnetic properties and insulating character of the quasi-one-dimensional AF Li_2CuO_2. Due to the formation of a strongly hybridized, and energetically isolated, combination of d_{yz} and p_σ orbitals, a large moment is transferred to the O ions. A simple single-band system results, but one in which second neighbor coupling exceeds nearest neighbor coupling and the electronic and magnetic behavior is three dimensional.

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