Extended Moment Formation and Second Neighbor Coupling in Li₂CuO₂

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Comprised of ferromagnetic edge-sharing CuO₂ chains that order in antialigned fashion at T_N=9 K, Li₂CuO₂ is found from local spin density calculations to display several surprising characteristics: (1) the ordered moment/f.u. of 0.92 μB 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 the largest oxygen moment yet reported, and (3) the second neighbors couplings are larger than nearest neighbors couplings. All of these phenomena arise naturally due to a well defined effective d_xy type orbital that includes very strong O pₓ character. We interpret the large moment as surviving reduction by quantum fluctuations due to extension caused by the d – p hybridization.

Low dimensional (1D or 2D) spin S=1/2 materials are critical systems displaying a variety of phenomena in crystals. These range from spin gap behavior in Ca₃V₄O₉ to anomalous spin physics in the one-dimensional spin chains and ladders. Many of these characteristics depend crucially on specific structural or chemical bonding features. 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) CuO₄ 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 Tc planar compounds and Sr₂CuO₃), edges (as in CuGeO₃, La₆Ca₈Cu₂₂O₄₁, and Li₂CuO₂), or both (as in SrCuO₂). In edge sharing CuGeO₃, for example, there is moderately strong antiferromagnetic (AF) nn coupling (J≈150 K), but a spin-Peierls transition occurs only at 14 K. The typical example of corner-sharing chains is Sr₂CuO₃, where the system orders antiferromagnetically with a low transition temperature of 5 K and a small induced magnetic moment (0.06 μB) in spite of very large interactions between ions (J≈2200 K). Despite considerable progress a clear understanding of the magnetic behavior of the Cu²⁺ ion in several regimes is still lacking.

Here we report a new aspect of spin behavior in edge-sharing systems revealed by spin-polarized local density approximation (LDA) studies of a 1D S=1/2 system Li₂CuO₂. In this compound neutron scattering indicates three dimensional AF ordering at 9 K arising from the antialignment of FM chains. The experimental moment of 0.9 μB per cell was attributed completely to the Cu ions. Based upon experience in the undoped two-dimensional cuprates (viz. La₂CuO₄) where LDA is unable to obtain any moment whatsoever on the Cu ion, it might seem that LDA is unlikely to produce a magnetic Cu ion or an insulating system. Due to this problem with corner-sharing Cu-O planes, very few spin-polarized calculations on cuprate compounds have been reported. However, we find that LDA predicts Cu in Li₂CuO₂ 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 μB per atom, the largest O moment yet reported. Previous reports of O moments lie in the 0.02-0.10 μB range.

Li₂CuO₂ is orthorhombic and belongs to the category of edge-sharing compounds, with one-dimensional CuO₂ 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 φ = 94°, intermediate between the two other edge-share compounds with very different characteristics: GeCuO₃ (spin-Peierls, φ = 99°) and La₆Ca₈Sr₂₀O₄₁ (FM, φ = 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, which makes no shape approximations for the density or potential. 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...
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 CuO2 edge-sharing compounds CuGeO3 [11] and NaCuO2. [14] 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 only Cu d$_{yz}$-O $p_\sigma$ (the $p_y \pm p_z$ combination directed towards the Cu site) are present in this band.

The geometry of this CuO2 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 in a primitive cell can be chosen as the Cu d orbitals, the $\sigma$-type O $p_\sigma$ 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 that are non-bonding and lie well below the Fermi level (as do all d orbitals except d$_{yz}$). The $p_\sigma$ orbitals in the $y - z$ plane of the ribbon are $p_\sigma$ with respect to a neighboring Cu and belong to the next unit cell. The d$_{yz}$ and the four $p_\sigma$ orbitals can be decomposed into five hybridized combinations: one bonding combination $D_{yz}^\sigma$ and one antibonding combination $D_{yz}^\pi$ of d$_{yz}$ and the combination of the four $p_\sigma$ orbitals with d$_{yz}$ symmetry, and three other $p_\sigma$-only combinations of lower symmetry. $D_{yz}^\sigma$ and $D_{yz}^\pi$ are split strongly, leaving $D_{yz}^\pi$ at the Fermi level and $D_{yz}^\sigma$ 5 eV below, as shown in the density of states plot in Fig. 3. The others lie around -4 eV below the Fermi level and are not of interest. The general behavior of the coupled d$_{yz}$ - $p_\sigma$ cluster can be modelled with $\epsilon_d = -1.5, \epsilon_p = -4, (dp\sigma) = \pm 1.15, (pp\sigma) = 0.25$, (all in eV). For these parameters the $D_{xy}^\pi$ density is 70% on the Cu and 30% on the four O ions.

The active orbital $D_{yz}^\pi$ shown (schematically) as $|D_{yz}^\pi|^2$ on next nearest neighbors in Fig. is an effective $d_{yz}$-type orbital centered on each Cu ion but extending strongly to the neighboring O sites. Symmetry allows direct $DD\pi$ overlap, and therefore hopping amplitude $t_\pi$ 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 ($\phi = 90^\circ$) the O $p_\sigma$ orbitals directed toward the two neighboring Cu ions would be precisely $p_y \pm p_z$. These combinations are orthogonal, so $t_\pi$ reduces to direct d-d overlap and will be very small. When the Cu-O-Cu angle is not exactly 90°, the $p_\sigma$ orbitals are no longer orthogonal and the overlap (and $t_\pi$) increases.

The effective Hamiltonian therefore reduces to a single orbital ($D_{yz}^\pi$) per cell. The dispersion of the $D_{yz}^\pi$ band cannot be fit simply by nn hopping $t_\pi = t_1$ along the chain and $t'_1$ between neighboring chains (in roughly the $\pm \hat{x}$ directions), but requires as well both next nearest neighbor (nnn) hopping terms $t_2$ and $t'_2$. Consideration of the $D_{yz}^\pi$ 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

$$nn : \quad t_1 = -63 \text{ meV}, \quad t'_1 = -16 \text{ meV},$$
$$nnn : \quad t_2 = -94 \text{ meV}, \quad t'_2 = 44 \text{ meV},$$
The moment of 0.92 \( \mu_B \) 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 \( \mu_B \) on each O) is to our knowledge the strongest yet reported in a transition metal oxide compound [14].

Previous reports of moments lie in the 0.02-0.10 \( \mu_B \) range. [1] To illustrate the importance of the O sites, we display the exchange potential \( V_1 - V_2 \) for the ferromagnetic and antiferromagnetic chains in Fig. 4. There is a clear similarity, especially for the AF chain, to the \( D_{yz}^* \) 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 \( D_{yz}^* \) 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 \( \mu_B \)) is essentially independent of the overall magnetic ordering.

Antialignment of FM chains leads to the insulating band structure shown in Fig. 2c. 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 \( \Delta = 0.8 \text{ eV} \) is the exchange splitting evident in Fig. 2c. Since \( \Delta \) is much greater than all of the hopping amplitudes and in fact similar to the PM bandwidth, the exchange coupling between the antialigned chains results in very narrow band splits by \( \Delta \).

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, [1] although the moment there was...
attributed solely to Cu. This is a remarkably large value for a quasi-1D S=½ chain, where quantum fluctuations should be large. The strong nnn coupling that we have uncovered account for the observation qualitatively: coupling between the $D_{yz}^*$ effective orbitals, and therefore the spins, is really three dimensional, hence quantum fluctuation effect are vastly reduced.

Recently two similar compounds with one-dimensional chains have been reported. Both Sr$_{0.73}$CuO$_2$ and Ca$_{0.85}$CuO$_2$ have CuO$_2$ ribbons and order magnetically. Comparison with Li$_2$CuO$_2$ is difficult, however, because the strongly differing doping level and the structural disorder can lead to large changes in the magnetic behavior. Recent work on the Ca$_{2+x}$Y$_{2-x}$Cu$_5$O$_{10}$ is suggestive, since susceptibility measurements are interpreted as indicating that each extra doped hole creates a (non-magnetic) Zhang-Rice singlet. Our results for Li$_2$CuO$_2$ suggest that for the edge-sharing chains each extra hole occupies a $D_{yz}^*$ orbital and therefore is weakly coupled to neighboring Cu ions. In this case the Cu ion and four neighboring p$_x$ orbitals would be non-magnetic, rather than having a Cu spin be compensated by neighboring O spins. Further experiments will be necessary to test our picture.

To summarize, we have found that LDA provides a consistent picture of the magnetic properties and insulating character of the quasi-one-dimensional antiferromagnet Li$_2$CuO$_2$. Due to the formation of a strongly hybridized, and energetically isolated, combination of $d_{yz}$ and p$_x$ orbitals, a large moment is transferred to the O ions. A simple single-band system results, but one in which second neighbors coupling exceeds nearest neighbors coupling and the electronic and magnetic behavior is three dimensional.

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