Electronic structure and magnetism of the "pseudo-ladder" compounds ACu$_2$O$_3$, A = Ca,Mg

S.-L. Drechsler a,*, H. Rosner b, T.K. Kim a, M. Knupfer a, J. Málek a,1, H. Eschrig a

a Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, P. O. Box 270116, D-01171 Dresden, Germany
b Max-Planck-Institut für Chemische Physik Fester Stoffe, Dresden, Germany

Abstract

The electronic structure of ACu$_2$O$_3$ compounds [A = Ca,Mg] has been calculated within the local density approximation (LDA) and compared with recent magnetic neutron scattering data. Both compounds deviate markedly from the usual $pd_{\Gamma}$ cuprate picture. Strong interlayer exchange is found to be responsible for the missing spin gap generic for ideal two-leg ladders (TLL). Hence, they can be modelled as weakly coupled anisotropic bilayers.

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Cuprate based spin-ladder compounds have been intensively studied in last years [1]. Two-leg pseudo-ladders (TLPL), such as LaCuO$_2$$_5$ and the title compounds, constitute a seemingly related group. However, their magnetic ordering at low temperatures $T$ suggests a position in between highly anisotropic nearly 1D corner-shared antiferromagnetic (afm) CuO$_3$ chain compounds and less anisotropic materials with more or less comparable interacting strength of CuO$_4$ plaquettes in all directions. In contrast to weakly interacting TLL with a spin gap and $\mu = 0$ in a spin-liquid ground state, strongly interacting TLPL exhibit 3D Neél order at $T < T_N$ with $\mu \neq 0$, like unfrustrated single-chain compounds without spin-Peierls transition. Here, we will give some insight in the origin of the behavior of known TLPL which can be first characterized as: LaCuO$_2$$_5$ ($T_N \approx 117 \pm 17$ K, $\mu = 0.5 \pm 0.2\mu_B$ [2]), MgCu$_2$O$_4$ ($T_N \approx 95$ K, $\mu = 0.32 \pm 0.02\mu_B$ [3]), and CaCu$_2$O$_3$ ($T_N \approx 27$ to 25 K, $\mu = 0.2 \pm 0.07\mu_B$ [4,5]). Below $T_N$ the isostructural title compounds (which can be viewed as stacked buckled Cu$_2$O$_3$ planes of the prototypical planar TLL SrCu$_2$O$_3$ system (see Fig. 1)) show besides common afm period doubling along the chain ($b$-axis), different magnetic structures in $c$ and $a$-directions: ferromagnetic (fm) ordering in $c$-direction and on the kinked PL-rungs for A = Mg, and afm ordering for A = Ca. Along the $a$-axis afm period doubling and/or an incommensurate spiral-type wave near 3/7 commensurability, respectively, have been observed. Ongoing from SrCu$_2$O$_3$ with straight rungs to strongly "kinked" rungs in MgCu$_2$O$_3$ and beyond, with decreasing buckling (Cu–O–Cu bond) angle $\Theta$ there is a transition from a superexchange dominated afm to a fm rung exchange (governed by Hund’s rule coupling at the intermediate O of the rung centre) approaching $\Theta = 90^\circ$, provided the crystalline field caused splitting of onsite energies for differently oriented O 2p orbitals is small. Comparing the observed magnetic structures one concludes that this transition occurs at a critical $\Theta_c$ in between those of A = Ca and A = Mg. Near $\Theta_c$ the rung exchange $J_r$ should be small.

In order to quantify the afm contributions we analyzed the dispersions of bands near the Fermi energy $E_F$.
obtained from full potential LDA calculations with the FPLO code. For details see Ref. [6]. A justification for the LDA based electronic structure is the reasonable description of the unoccupied electronic states for A = Ca probed recently by polarization dependent X-ray absorption spectroscopy [6]. Since the exchange along a is frustrated due to the shift of the nearest neighbor TLPL by 0.5 \( b \) along \( b \), only a weak afm exchange \( J_a \) results (compare e.g. the weak dispersions along \( I'X \) in both panels of Fig. 2) from the unshifted second neighbor pseudo-ladder. Ignoring that frustration as well as a weak rung exchange \( J_r \) as first suggested in Ref. [4], this leads to a spatially anisotropic Heisenberg problem with a hierarchy of exchange integrals \( J_b \sim J_a \sim J_c \). Hence, at \( T = 0 \) the magnetic order can be described within an effective 2D-model for interacting chains in the \( b-c \) plane. With Sandvik’s 2D mean-field result for \( \mu \) (in units of \( \mu_B \)) at \( T = 0 \) [7]

\[
\mu = 0.273g_L \sqrt{1/\gamma (1 + 0.095/\gamma)} \ln^{1/3} (1.3\gamma),
\]

we estimate from the mentioned \( \mu \)-values the exchange anisotropy: \( \gamma \equiv J_b/J_a \approx 6 \pm 0.9 \) (A = Mg) and 20 (50 to 9) (A = Ca), where a Landé factor \( g_L = 2.2 \) has been adopted. With \( J_b = 1540 \) and 2000 K [3,4] we arrive at \( J_a(Mg) = -22.1 \) meV and \( J_a(Ca) = +8.6 \) meV with signs chosen according to the experimental magnetic structures. Note also the approximate relation \( T_N \propto |J_c| \), typical for quantum spin chains [8,9]. We decompose the \( J_c's \) into afm and fm contributions. From effective transfer integrals \( t_e \) derived from the dispersions parallel to \( c \) (\( ITZ \) in Fig. 2) and a typical Hubbard \( U = 4 \) eV, one arrives at \( J_{c,\text{afm}}(Ca) = 4 t_e^2/U = 17.6 \) and 36.6 meV for

\[ A = \text{Mg}. \]

Then markedly different empirical fm contributions result: \( J_{c,\text{fm}} = -58.7 \) for A = Mg and \( -9.4 \) meV for A = Ca. A similar total fm interladder coupling of about \( -10 \) meV has been estimated for LaCuO\(_2\) [10]. Mixed crystals Ca\(_{1-x}\)Mg\(_x\)Cu\(_2\)O\(_3\) allow a smooth transition between the two limiting crystal structures. In our view, at some critical concentration \( x_c \) (buckling angle) \( J_r \) changes its sign. Near \( x_c \) the ideal TLL picture with vanishing \( T_N(x) \) and \( \mu(x) \) might be retained, if \( J_a \ll |J_c| \) holds. Otherwise, minima of \( T_N(x) \) and \( \mu(x) \) are expected. Notably, a shallow minimum of \( T_N \) has been reported for \( x \approx 0.2 \) [5].

To summarize, the magnetism of both title compounds is governed by sizable exchange in \( c \)-direction which destroys the usual TLL-picture.

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References

A simple analysis of their data is hampered by some inherent disorder and nonstoichiometry.

For the calculation of $A = \text{Mg}$, $\text{Mg 3s, 3p, and 3d valence states were used.}$