Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Magnetism and Magnetic Materials 290-291 (2005) 345–348
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

# Spiral vs. ferromagnetic in-chain order in edge-shared cuprates

S.-L. Drechsler[a,*], J. Richter[b], J. Málek[c], A.S. Moskvin[d], R. Klingeler[a], H. Rosner[a,1]

[a] *Leibniz-Institut f. Festkörper-und Werkstoffforschung IFW Dresden, P.O. Box 270016, Dresden 01171, Germany*
[b] *Institut für Theoretische Physik, Universität Magdeburg, Magdeburg, Germany*
[c] *Institute of Physics, ASCR, Prague, Czech Republic*
[d] *Ural State University, Ekaterinburg, Russia Federation*

Available online 15 December 2004

**Abstract**

Different magnetic ground states of structurally similar compounds bearing edge-shared $CuO_2$ chains are explained within a common approach in terms of frustrated single-chain couplings and antiferromagnetic interchain exchange.
© 2004 Elsevier B.V. All rights reserved.

*PACS:* 75.10.Pq; 75.25.+z; 75.30.Kz

*Keywords:* Edge-shared cuprate chain; Quantum helix

Undoped edge-shared $CuO_2$ chain bearing compounds exhibit a surprisingly large variety of magnetic ground states (GS). Thus, near 9 K the prototypical $Li_2CuO_2$ shows a transition to a (commensurate) Néel state dominated by antiferromagnetic (afm) interchain coupling but accompanied also by a ferromagnetic (fm) in-chain ordering, whereas the closely related $LiCu_2O_2$ [1,2] shows a transition to an incommensurate (IC) state along the chain direction $b$ below about 23 K, which probably represents a long sought spin-$\frac{1}{2}$ helix. Its details are still under debate, in particular two alternative frustrated models have been proposed and employed in the analysis of experimental data: (i) the "afm"-double chain (DC) or dimer liquid model [2–4]; and (ii) the fm–afm single-chain model [1]. By neutron scattering, Masuda et al. observed a corresponding propagation vector $\zeta = 0.1724$ (in units of the reciprocal lattice vector $2\pi/b$ in chain direction) and nonequivalent Bragg reflexes near integer values $k \pm \zeta$ similar to $\zeta = \frac{1}{8}$, $l = l_0 \pm \frac{1}{8}$, $l_0 = 0, 1$ reported for $SiCuO_3$ below 8 K [5]. Therefore, we suggest a helix also for $SiCuO_3$. A similar IC state has been proposed for $Rb_2Cu_2Mo_3O_{12}$ based on magnetic susceptibility data [6]. Finally, $CuGeO_3$ with the afm nearest (nn) neighbor exchange shows a spin-Peierls GS supported by frustrating afm next-nearest neighbor (nnn) coupling. This disparity results from a complex interplay between the actual internal anisotropy of in-chain and off-chain transfer integrals governed by the Cu–O–Cu bond angle $\gamma \sim 90°$, the spin-anisotropy, the strength of the crystal field affected by the position and the charge of the cations and the interchain coupling. Here, we will focus on $Li_2CuO_2$ and $LiCu_2O_2$, adopting in the analysis the 1D isotropic frustrated spin-$\frac{1}{2}$ $J_1$–$J_2$ Heisenberg model with nn and nnn exchange.

## 1. Consequences of frustration in $CuO_2$ chains

With an afm nnn-coupling $J_2 > 0$ along a single $CuO_2$ chain, one is left with a frustration problem irrespective

*Corresponding author. Tel./fax: +49 351 4659 384(490).
*E-mail address:* drechsler@ifw-dresden.de (S.-L. Drechsler).
[1] MPI f. Chem. Physik fester Stoffe Dresden, Germany.

0304-8853/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2004.11.257

of the sign of $J_1$. For $Li_2CuO_2$, many experimental data are available. We fitted an extended Hubbard model to describe its optical conductivity and O 1s X-ray-absorption data. Then the lowest multiplet states (total spin $S = 0, 1, 2$) of periodic $Cu_nO_{2n}$ clusters with $n = 3$–6 were mapped onto $J_1$–$J_2$ Heisenberg rings with 3–6 sites to extract the exchange integrals. With respect to the small Cu–O–Cu bond angle $\gamma \approx 94^\circ$ there is consensus about the fm nature of $J_1$ for $Li_2CuO_2$ [7]. First principle LDA calculations [1] (see Table 1) and fits of the magnetic susceptibility result in $J_1 \approx -8$ to $-10$ meV for both compounds (for refinements for $Li_2CuO_2$, see below). Furthermore, there is a significant afm nnn exchange integral due to a non-negligible nnn transfer integral $t_{2y}$ leading to $\alpha = J_2/J_1 \sim -0.7$. However, such a large value of $\alpha$ clearly exceeds the well-known critical value of $\alpha_c^{1D} = -\frac{1}{4}$ for a spiral instability (independent of the actual spin value). This seemingly contradicts with experimental neutron scattering data, which show fm in-chain order can be resolved taking into account the specific interchain coupling in $Li_2CuO_2$ (see Section 2).

Another quantity of interest derived from experimental data is the Curie–Weiss temperature obtained from high-temperature susceptibility data according to $\chi(T) \propto 1/(T - \Theta_{CW})$ (see also Fig. 2).

## 2. Aspects of the interchain coupling

The interchain coupling is very sensitive to the chain arrangement in a real solid. In $Li_2CuO_2$ each $CuO_2$ chain is surrounded by four parallel nn chains shifted by half a lattice constant. Furthermore, the second neighbor transfer $J_\perp$ is of the same order as the first neighbor one $J'_\perp$. Thus, the effective number of nearest neighbors at surrounding chains is $z_{eff} = 16$! Treating the interchain coupling in mean-field theory and the in-chain coupling within the above-mentioned cluster approach one arrives for the high-temperature $\chi(T)$ at a simple Curie–Weiss law with

$$\Theta_{CW}^{3D} \approx \Theta_{CW}^{1D} - \frac{z_{eff} J_\perp}{4}, \qquad (1)$$

with $\Theta_{CW}^{1D}(\alpha)$ derived from numerically calculated $1/\chi(T)$ curves with $4|J_1| < T < 5|J_1|$. For results see Fig. 2. From Fig. 3, the observed Néel transition, LDA derived interchain couplings, and Eq. (1) for $Li_2CuO_2$ a tiny fm $\Theta_{CW}^{1D}$ can be conjectured (vanishing near $\alpha = 0.71$) [8]. Hence, the observed afm 3D value $\approx 30$–40 K is ascribed mainly to the afm interchain couplings. In contrast, for $LiCu_2O_2$ the value of $\Theta_{CW}^{3D}$ is determined both by the stronger afm nnn in-chain coupling $J_2$ and the weaker afm interchain coupling. In this bi-layer chain compound there are two nn chains within a single plane (see Fig. 1) and two nn chains within an adjacent plane in the bilayer. The so-called double-chains (DC) belong to adjacent bilayers. According to our LDA-calculation [1] both couplings are weak (compared with the main in-chain couplings) being of the same order, i.e. 0.5–1 meV. Thus, here $z_{eff} \sim 3$–4 is significantly smaller than in $Li_2CuO_2$.

To illustrate another specific interchain coupling feature in $Li_2CuO_2$, we consider the renormalized critical $\alpha_c^{3D}$. In contrast to the pitch angle [9], $\alpha_c$ is hardly affected by quantum (spin-$\frac{1}{2}$) effects like in the 1D and 2D cases [10,11] and we estimate the interchain

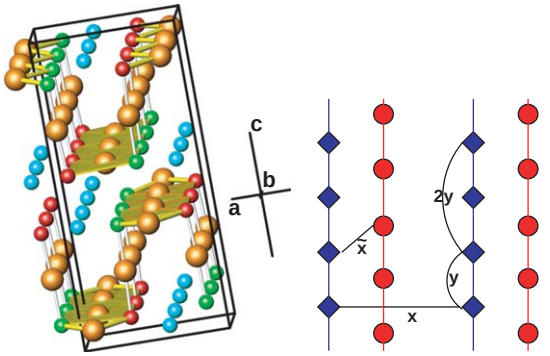


Fig. 1. The formal DC structure of $LiCu_2O_2$. Crystal structure with a DC along the $b(y)$-axis in the centre (left panel). Large ○ denote Cu sites. Projected bi-layer onto the $(a, b)$ plane with two DCs (right panel). ◆ and • denote the magnetically active Cu(2+) sites in different planes. Main exchange paths are denoted by off-chain lines.

Table 1
LDA hopping $t$ and exchange integrals $J$ in milli-electron-volt for $U = 3$ and 4 eV (in brackets); notation according to the right panel of Fig. 1. The total exchange integrals $J^{eff}$ consist of differently calculated afm and fm contributions: $J^{afm} = 4t^2/U$ (superexchange) and $J^{fm}$ (direct exchange) from Wannier-functions, respectively. The value of $U$ influences the $J^{fm}$'s via screening factors (here 3.3 and 2.46, respectively) [1]

| | $y$ | $2y$ | $x$ | $\tilde{x}$ | $xy$ |
|---|---|---|---|---|---|
| $\|t\|$ | 64 | 109 | 73 | 18 | 25 |
| $J^{afm}$ | 5.5 (4.1) | 15.8 (11.9) | 7.1 (5.3) | 0.4 (0.3) | 0.8 (0.6) |
| $J^{fm}$ | −13.6 (−17.9) | −1.4 (1.8) | −1.4 (1.8) | — | — |
| $J^{eff}$ | −8.1 (−13.9) | 14.4 (10.1) | 5.7 (3.5) | 0.4 (0.3) | 0.8 (0.6) |

effect on it within a classical spin model:

$$\alpha_c^{3D} = \alpha_C^{1D}(1 + \beta + 9\beta' + 25\beta'' + \cdots), \quad (2)$$

where $\beta = -J_\perp/J_1$, $\beta' = -J'_\perp/J_1$, and $\beta = -J''_\perp/J_1$, denote the 1st, 2nd, 3rd, respectively, exchange to a corresponding neighbor on an adjacent chain. The afm interchain $J_\perp \sim J'_\perp \approx 1$–$1.5$ meV is estimated from our LDA interchain transfer integrals $t_\perp$, via $J_\perp \approx 4t_\perp^2/U$, where $U \sim 4$ eV denotes the effective on-site Coulomb repulsion within a single-band model. Thus, one arrives at a strong enhancement of $\alpha_c$ by a factor of 3. As a result, our empirically and theoretically estimated single-chain frustration ratios $\alpha \approx -0.7$ are slightly above the expected renormalized $\alpha_c^{3D} \approx -0.75-0.8$ in accord with the absence of a helix in $Li_2CuO_2$. In addition, the ignored spin anisotropy further stabilizes the fm in-chain order. Our approach might explain the large fluctuations seen in various experiments due to the vicinity of the competing spiral phase/Lifshits point and not by strong 1D fluctuations as proposed [12].

In $LiCu_2O_2$, the interchain coupling (mainly within a DC) only weakly affects the critical value $\alpha_c^{3D}$. Here, the in-phase arrangement of chains slightly reduces the effective fm nn $J_1$. Only the weak coupling between chains in adjacent planes (shifted by $b/2$ along the $b$-axis, see Fig. 1) as in $Li_2CuO_2$, causes a renormalization of $\alpha_c^{3D}$ as in Eq. (2). However, in total its effect is reduced by a factor ~8 compared with $Li_2CuO_2$.

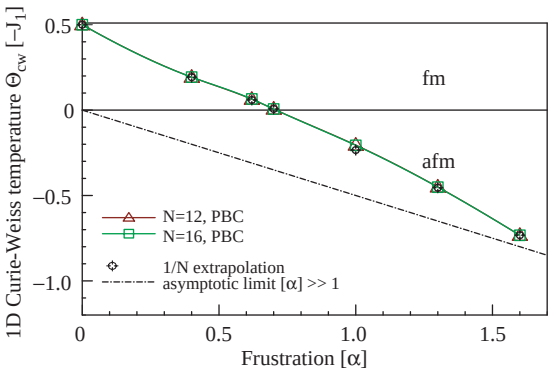


Fig. 2. The single-chain Curie–Weiss temperature $\Theta_{CW}^{1D}$ vs. nnn-exchange afm coupling (in units of fm nn-exchange) from the calculated $\chi(T)$ of frustrated spin-$\frac{1}{2}$ Heisenberg chains with periodic boundary conditions (PBC) with $N = 12$, 16 sites and a $1/N$ extrapolation to $N = \infty$. The dashed–dotted line denotes the behavior of decoupled afm chains approached asymptotically in the $J_2 \gg |J_1|$ limit.

## 3. Discussion and comparison with experiment

From cluster studies, we derived for frustrating afm $J_{nnn} > 0$ and $\alpha = -1.6$ an afm $\Theta_{CW,1D} \approx -71$ K. With $J_\perp \sim 10$ K [1] one arrives at the reported values of $\Theta_{CW} \approx -80$ to $-90$ K [3,13]. However, from the susceptibility $\chi(T)$ data shown in Fig. 3 we obtained a somewhat smaller $\Theta_{CW}^{3D} = -37$ K ($\mathbf{H}\|(a,b)$) and $-47$($\mathbf{H}\|c$), respectively, which together with the global fit of $\chi(T)$ results now in somewhat reduced values for $\alpha \approx -1$ and $\Theta_{CW}^{1D} = -19$ K. Then the effective interchain coupling amounts to 18 K (28 K) or 1.55 meV (2.4 meV) in accord with our LDA estimate. Concerning the susceptibility fits we note that the low-$T$ behavior is still affected by finite size effects. Interchain coupling, spin anisotropy, and a possible $T$-dependence of the $g$ factor [3] approaching the spiral transition should be taken into account to further improve the fit. For the closely related $Li_2CuO_2$ ($\alpha = -0.7$, $z_{eff} = 16$, and a fm $\Theta_{CW,1D} \approx +2$ K from the theoretical $\chi(T)$ (see Figs. 2 and 3)), adding the above-mentioned interchain couplings our model yields $\Theta_{CW} \sim -38$ K in accord with the experiment. With $\chi(T)$ from Refs. [7,12] one would arrive at $g \approx 2.04$–$2.1$.

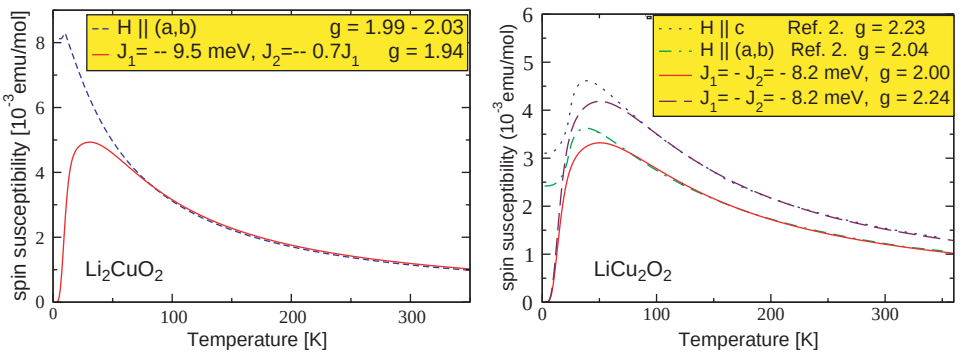


Fig. 3. Susceptibility $\chi(T)$ for spin-$\frac{1}{2}$ fm–afm Heisenberg rings with $N = 16$ sites (full (both panels) and bold dashed lines (right panel) compared with experiments (dashed (left panel), dotted and dashed–dotted lines (right panel)). The empirical Heisenberg $J$'s agree with microscopic ones from mapping low-lying magnetic excitations of the 5-band Cu 3d O 2p extended Hubbard model (fitted to spectroscopic data) onto excitations of the Heisenberg model.

To conclude, we have shown that the frustrated fm–afm single-chain model supplemented with LDA derived interchain coupling reveals a proper description of two typical edge-shared $CuO_2$ chain compounds. Although both materials exhibit comparable single-chain exchange couplings, $J_1 = -8.2$ and $-9.5$ meV, respectively, for nn's and $J_2 = 8.2$ and 6.6 meV for nnn's, respectively, $Li_2CuO_2$ is found to be close to a fm–afm helical ground state, still prevented by strong specifical, interchain coupling, whereas the long sought "fm" spin-$\frac{1}{2}$ helix is realized in $LiCu_2O_2$.

## Acknowledgements

The DFG (S.-L.D., J.M., and R.K. (SP 1073) and H.R. (Emmy-Noether-program)), INTAS (Grant 01-0654, A.M.) are acknowledged for their support. We thank H. Eschrig for useful discussions and A. Vasiliev and S.A. Zvyagin for providing us with $\chi(T)$ data of $LiCu_2O_2$. The results of the Heisenberg rings with $N = 16$ sites are obtained with J. Schulenburg's SPIN-PACK.

## 4. Note added in proof

Recently, for two closely related edge-shared $CuO_2$ chain based compounds spirals of the same single chain fm-afm frustration origin as discussed above have been discovered:

$LiVCuO_4$ (B.J. Gibson et al., Physica B 354 (2004) e253) and $NaCu_2O_2$, isomorphic with $LiCu_2O_2$ (L. Capogna et al. cond-mat/0411753). Concerning the present state of the debate on $LiCu_2O_2$, see also the comment S.-L. Drechsler et al. cond-mat/0411418 and the reply by T. Masuda et al. cond-mat/0412245 (Phys. Rev. Lett (2005) in press) as well as their extended preprint cond-mat/0412625.

## References

[1] A.A. Gippius, et al., Phys. Rev. B 70 (2004) R01426.
[2] T. Masuda, et al., Phys. Rev. Lett. 92 (2004) 177201.
[3] S. Zvyagin, et al., Phys. Rev. B 66 (2000) 064424.
[4] K.-Y. Choi, et al., Phys. Rev. B 69 (2004) 104421.
[5] H. Wolfram, et al., Phys. Rev. B 69 (2004) 144115.
[6] M. Haase, et al., cond-mat/0404463.
[7] Y. Mizuno, et al., Phys. Rev. B 57 (1998) 5326.
[8] The very existence of a zero for $\theta_{CW}$ for a single fm–afm chain is obvious from the two limiting cases: (i) for $J_2 \gg -J_1$ one approaches the case of two decoupled afm chains with $\theta_{CW} = -0.5J_2 < 0$ but (ii) in the opposite limit one tends to $\theta_{CW} = -0.5J_1 > 0$ (fm single-chain).
[9] R. Bursill, et al., J. Phys. C 7 (1995) 8605.
[10] V.Ya. Krivnov, et al., Phys. Rev. B 53 (1996) 6435.
[11] S. Krüger, J. Richter, Phys. Rev. B 64 (2001) 024433; S.E. Krüger, J. Richter, J. Schulenburg, D.J.J. Farnell, R.F. Bishop, Phys. Rev. B 61 (2001) 14607.
[12] S. Ebisu, et al., J. Phys. Chem. Solids (1998) 1407.
[13] Notice the + sign convention of $\Theta_{CW}$ used in Ref. [3].