The route of frustrated cuprates from antiferromagnetic to ferromagnetic spin-1/2 Heisenberg chains: Li$_2$ZrCuO$_4$ as a missing link near the quantum critical point

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From thermodynamics, LSDA+$U$ studies and exact diagonalizations of a five-band Hubbard model on CuO$_2$ stripes we found that Li$_2$ZrCuO$_4$ (Li$_2$CuZrO$_4$ in traditional notation) is close to a ferromagnetic critical point. Analyzing its susceptibility $\chi(T)$ and specific heat $c_p(T,H)$ within a Heisenberg model, we show that the ratio of the 2nd to the 1st neighbor exchange integrals $\alpha=-J_2/J_1$ -0.3 is close to the critical value $\alpha_c$=1/4. Comparing with related chain cuprates we explain the rather strong field dependence of $c_p$, the monotonous down shift of the peak of $\chi(T)$, and its increase for $\alpha\rightarrow\alpha_c+0$.

The one-dimensional (1D) spin-1/2 antiferromagnetic (AFM) Heisenberg model (HM) is one of the most studied many-body models in theoretical physics. Much of its physics is now well understood based on the rigorous Bethe-Ansatz method for infinite chains 1 and on finite cluster calculations. Thermodynamic benchmarks of this model relevant here are: (i) single maxima of the spin susceptibility $\chi(T)$ and specific heat $c_p(T,H)$ within a Heisenberg model, we show that the ratio of the 2nd to the 1st neighbor exchange integrals $\alpha=-J_2/J_1$ -0.3 is close to the critical value $\alpha_c$=1/4. Comparing with related chain cuprates we explain the rather strong field dependence of $c_p$, the monotonous down shift of the peak of $\chi(T)$, and its increase for $\alpha\rightarrow\alpha_c+0$.

\[ \text{Hamiltonian } H = \sum_{i} J_1 S_i S_{i+1} + J_2 S_i S_{i+2} + J_3 S_i S_{i+3} + \ldots \] 

has also attracted attention due to the frustration caused by AFM $J_2$, irrespective of the sign of $J_1$. If the $J_i$ are AFM, the frustration may cause a spin gap, e.g. for $J_2/J_1 > 0.241$ and $J_i = 0$, $i \geq 3$ (adopted mostly below). It strongly supports a dimerized ground state in spin-Peierls chains such as in GeCuO$_3$ 8. Recently, FM-AFM analogs realized in most edge-shared chain cuprates have caused attention with respect to strong quantum effects 4, to unusual thermodynamics of the disordered phase 5,6, and to helicoidal ground states found in some chain cuprates at low $T$ 5,8,9,10,11,12,13,14,15,16,17. However, issues like the behavior at very low $T$ and in magnetic fields near the critical point $\alpha_c = -J_2/J_1 = 1/4$ are still unclear and difficult to study numerically 6 even by the transfer matrix renormalization group (TMRG) method. For $\alpha > \alpha_c$, the ground state of a classical chain is formed by a helix with a pitch angle $\phi$ given by $\cos \phi = -J_1/4J_2 \equiv 1/(4\alpha)$. This helix interpolates between a FM-chain at $0 \leq \alpha \leq \alpha_c$ and two decoupled AFM-chains at $\alpha = \infty$. Noteworthy, $\alpha_c$ is unaffected by quantum effects 17. Since this should hold for the case of long-range inchain couplings, too, we expect a down(up)shift of $\alpha_c$ for AFM (FM) $J_i$, $i \geq 3$:

\[ \alpha_c = \frac{1 + 2.25J_3}{J_2} + 4J_4 + \frac{2.25}{J_2} + \frac{9}{J_2} + \ldots \] 

Recently, low $T\chi(T)$ data for Rb(Cs)$_2$Mo$_3$Cu$_2$O$_{12}$ 10 have been refitted by the isotropic $J_1$-$J_2$ HM near $\alpha_c$. However, both compounds seem to be affected by Dzyaloshinskii-Moriya interactions $D_{ij}(S_i \times S_j)$ 18 and exhibit a very complex, partially unresolved crystal structure, complicating a theoretical study even more.

Hence, studies of less complex systems described by Eq. (1) but with $|\alpha - \alpha_c| < 1$ are of general interest. Analyzing $\chi(T)$, $c_p(T,H)$, and the electronic structure of Li$_2$ZrCuO$_4$ we will show that it is a suitable candidate to probe the vicinity of $\alpha_c$ from the helical side. Together with data for related systems with $\alpha \geq 1$ it provides a so far missing link near $\alpha_c$ to study e.g. the $\alpha$-dependence of relations (i)-(iii), moving from AFM to FM-chains.

The orthorhombic crystal structure of Li$_2$ZrCuO$_4$ 18 (space group Cccm) with the lattice constants $a=9.385$ Å, $b=5.895$ Å, $c=5.863$ Å is shown in Fig. 1. Here chains (formed by flat edge-shared CuO$_4$ tetrahedra like the edge-sharing of CuO$_4$ plaquettes in other chain cuprates) run along the c-axis. Also the Cu-O bond length of 2.002 Å and the Cu-O-Cu bond angle $\gamma = 94^\circ$ resemble those with FM $J_1$. 

\[ a = 9.385 \text{ Å}, \quad b = 5.895 \text{ Å}, \quad c = 5.863 \text{ Å} \]
FIG. 1: (Color online) Crystal and electronic structure near the Fermi level $E_F=0$ of Li$_2$ZrCuO$_4$. Left: Crystal structure. Cu$^{2+}$- large orange ○, Zr$^{4+}$- light magenta ○ inside the magenta corner-shared ZrO$_6$ octahedra, red ○- O$^{2-}$, and light blue ○- Li$^+$ (Li (split) positions near Zr are omitted for clarity); the nonplanar edge-shared CuO$_2$ chains (olive-green). Right: LDA-FPLO band structure (c) and TB fit (red line). Γ-X-Y-Z-S are symmetry points in wave vector notation: (0,0,0);(2π/a,0,0);(0,2π/b,0);(0,0,2π/c);(2π/a,2π/b,0), respectively.

The $\gamma$-polymorph of Li$_2$ZrCuO$_4$ (Li ordered) was prepared by a solid state reaction of Li$_2$CO$_3$, ZrO$_2$ and CuO [18]. The reagents were mixed in an agate mortar and fired for a few hours in a Pt boat at 700°C to decarbonate them. Final firing of the pellet was performed at 1050°C for 24 h in a flow of O$_2$ followed by furnace cooling in O$_2$. Phase purity was confirmed by x ray diffraction.

The magnetization of Li$_2$ZrCuO$_4$ measured in a range $2\leq T \leq 350$ K for 0.1 T by a Quantum Design SQUID magnetometer is shown in Fig. 2. From the observed $T_N^\parallel \approx 7.6$ K one might at first glance expect an AFM spin liquid regime with $J_1$ or $J_2 \approx 12$ K, if $\gamma$ is just by chance close to that bond angle where $J_1$ changes its sign and either $J_1 \gg J_2 > 0$ due to the non-ideal chain geometry or vice versa $J_2 \gg |J_1|$. But the measured $\chi^*(T_m)$ is twice as large as the AFM-HM value of 0.1469 ($\chi^{AFM-HM}(T_m)$=0.0183 emu/mole for $g=2$). $1/\chi(T) \propto T + \Theta_{CW}$ reveals a FM Curie-Weiss temperature $\Theta_{CW} = -24$ K using a narrow temperature range near 350 K. Both facts exclude any AFM-HM like scenario. But they point to FM exchange involved in accord with fits by the $J_1$-$J_2$ model (Fig. 2).

Specific heat down to 0.35 K was measured by Quantum Design Physical Properties Measurements System (see Fig. 3). It shows a relative sharp peak near 6.4 K at $H = 0$. Using $c_p \approx c_v \equiv c$ [20], the observed ratio $T_{m\parallel}^\perp/T_{m\parallel}^\parallel = 1.17$ differs from 1.33 predicted by the AFM-HM. Note that $T_{m\parallel}$ nearly coincides with the $T$ for which $d\chi(T)/dT$ becomes maximal. Hence, it is unclear whether can this peak be attributed either to a $c_p$ anomaly indicating often a magnetic phase transition [21], or to a specific feature of the disordered phase for the 1D frustrated $J_1$-$J_2$ HM at $\alpha_{\perp} < \alpha < 0.4$ . Here $c_v$ exhibits a two-peak structure [22, 23]: a sharp peak at low $T$ under consideration and a broad one at high $T$ hidden in the phonon region ($k_BT \sim 0.65 |J_1| \approx 260$ K in the present case). Anyhow, with increasing field $T_{m\parallel}$ is downshifted and $c_p(T_{m\parallel})$ is suppressed but $c_p(T)$ increases rapidly for $T \geq 12$ K, well above a possible phase transition near 6K.

A similar strong $H$-dependence is found in full diagonalization studies of large rings, where the low-$T$ peak is first downshifted with increasing $H$ and upshifted at higher $H$ (Fig. 4). The strong $H$-dependencies of both $\Delta \chi(H)-\chi(0)$ and $\Delta T_{m\parallel}^\perp/T_{m\parallel}^\parallel = T_{m\parallel}^\perp(T_{m\parallel}^\parallel - H^2)$ already at weak fields $H \ll 9T$ result from the vicinity to $\alpha_c$ [22]. Adding a usual lattice contribution $c_{lat} \propto T^3$ ($\Theta_D=220$ K) to the calculated spin specific heat within the isotropic $J_1$-$J_2$ HM the experimental data are best described by $\alpha = 0.3$ (Fig. 4). From the low $H$-crossing point near 12 K we estimate $J_1 \approx 405$ K to $\sim 363$ K using the $\chi(T)$ data for $\alpha = 0.29$. The low-$T$ peaks ex-

FIG. 2: (Color online). Magnetic susceptibility of Li$_2$ZrCuO$_4$ together with fits by the $J_1$-$J_2$ model for periodic chains.

FIG. 3: (Color online) Specific heat $c_p$ of Li$_2$ZrCuO$_4$ vs. $T$ at various external magnetic fields $H$. Inset: the same for $c_p/T$. 
1D magnetic approach is a reasonable starting point despite the more 2D electronic structure seen e.g. along the symmetry lines Γ-Y and S-X in Fig. 1.

To get insight into the J-set obtained above, we performed calculations of the electronic and magnetic structure within the local (spin) density approximation (L(S)DA). In addition, LSDA+U calculations and exact diagonalizations for an appropriate extended multiband Hubbard model were carried out to take the strong correlations for the Cu 3d holes into account. The LDA calculations (Perdew-Wang92 parametrization) were performed using the full-potential local-orbital minimum-basis scheme (FPLO, vers. 5.00-19) [23]. We employed a basis set of Cu(3s3p):(4s4p3d), O(2s2p3d), Zr(4s4p):(5s5p4d), and Li(1s):(2s2p3d). For the LSDA+U in the AFM version [24] we used \( U_{3d}=6.5\pm1.5 \) eV and the intraatomic exchange \( J_{ex}=1 \) eV. Following the approach of analyzing total energy differences for various magnetic superstructures [23], we obtain \( J_1=-151\pm35 \) K and \( J_2=35\pm12 \) K. Using a typical one-band Hubbard \( U_{eff}=1.5 \) eV as well as \( t_2 \) and \( t_3 \) from the TB fit of the band at \( E_F \) (Fig. 1) results in \( J_3=46 \) K and \( J_3=6 \) K employing \( J_1=4t_2^2/U \), both close to \( \alpha_c=0.195 \) in the present case of \( J_3 \neq 0 \) (s. Eq. (2)).

Finally, a collection of known \( T_{N}/J_2 \) and \( \chi(T) \) values from other chain cuprates we derived from their \( \chi(T) \) data [10] to [12], is shown in Fig. 5 [27]. In particular, it is clear why the large-\( \alpha \) chains in SrCuO\(_2\) and LiVCuO\(_4\) are often regarded as AFM-HM archetypes [28]. Only after the discovery of spirals, detailed inelastic neutron scattering studies, and our three component

![Image](https://via.placeholder.com/150)

**FIG. 5:** (Color online) Empirical \( T_N/J_2 \) in units of the fitted \( J_2 \) value of the FM-AFM \( J_1,J_2 \) model for several frustrated chain cuprates (black squares): 0- \( \alpha_c=1/4 \), 1- Li\(_2\)ZrCuO\(_4\), 2- Pb\(_2\)CuSO\(_4\)(OH)\(_2\), 3- Rb\(_2\)Cu\(_2\)Mo\(_2\)O\(_8\), 4- Cs\(_2\)Cu\(_2\)Mo\(_2\)O\(_8\), 5- LiCu\(_2\)O\(_2\), 6- NaCu\(_2\)O\(_2\), 7- LiVCuO\(_4\), and 8- SrCuO\(_2\). The measured pitch is given in brackets. The filled green o denote the full diagonalization results of the \( J_1,J_2 \) model on rings with \( N=20 \) sites. Inset: the maximum value of \( \chi(T) \).
theoretical analysis (HM, Cu-O Hubbard model, LDA) initial assignments for LiVCuO4 and LiCu2O2 were corrected. Similarly, among systems assigned so far as "perfect" realizations of the AFM/FM HM (e.g. ZrCuO2) could be further J1-J2 candidates worth to be revisited. Similar plots which accent the FM critical point can be made also for the low-T peak of c0 or χ(0) (which monotonously increases and diverges finally as α → αc).

We expect that a vanishing χ(c) and a diverging χ(T) for T → 0 in approaching αc are generic for a FM critical point. It should hold also for models beyond the J1-J2 HM. Further couplings do affect the helical phase in changing e.g. the pitch and αc (see Eq. (2)).

Comparing α ∼ αc for Li2ZrCuO4 with α ≫ αc we found for other chain cuprates the question arises, what is the microscopic reason for? There are at least two options: (i) an enhanced | J1 | at a standard J2 value and vice versa (ii) a slightly enhanced | J1 | at a reduced J2. Case (i) can be ascribed to enhanced FM contributions to J1 which arise from the direct exchange Kpd or from the Hund's rule coupling at the sharing O ions within a five-band Cu 3d O 2p extended Hubbard model. Unfortunately, there is no generally accepted Kpd value; but it is the most sensitive quantity for the determination of J1 in edge-shared cuprates. Nevertheless, usually Kpd is treated as a fit parameter: The well-studied Li2CuO3 can be described with Kpd=50 meV [32], whereas microscopic calculations for La2CuO4 yield 180 meV [32] and a structural analysis of GeCuO3 was performed assuming Kpd=110 meV [31].

Within the Cu 3d|yz O 2p|yz,pz extended Hubbard model for planar CuO2 n+1 open chains (n ≤ 5), we adopted Kpd=70 meV. From a direct mapping onto the J1-J2 HM using two O site energies Δp|y,z=2.7meV and Δp|z=3.2eV as well as LiCuO2-like parameters, we found J1=317 K, J2=90 K, and α =0.284, close to our empirical values. In case (ii) supported by the LSDA+U results, we arrive also close to αc. Here J2 amounts 46 K, only. From a comparison with other cuprates in Fig. 5 more insight will be gained into the nature of the exchange in cuprates and into the novel physics generated by a quantum FM critical point.

To conclude, we have shown that a growing number of edge-shared chain cuprates form a special family which thermodynamics can be described within the J1-J2 model with FM NN and AFM NNN exchange. Moving from the AFM-HM towards αc, almost achieved for Li2ZrCuO4, observed monotonous changes can be explained. Only chains near the FM critical point show peculiar physical properties such as the strong H-dependence of c0 in a large T range reported here. Further studies of Li2ZrCuO4 at very low T, under pressure, and in high fields are highly desirable. If the observed c0-peak is related to magnetic ordering, neutron diffraction below 6 K should reveal a spiral with a pitch below the minimum value of 62° observed so far among edge-shared chain cuprates for LiCu2O2.

Inelastic neutron scattering studies might be helpful to refine the exchange integrals, especially with respect to the interchain coupling.

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[^19]: We use Li2ZrCuO4 and GeCuO2 instead of Li2CuZrO4 and CuGeO3 and analogously for other edge-shared systems to accent their cuprate (not zirconate or germanate, etc.) nature. A more precise, but somewhat lengthy, notation would be Li2Zr2O3Cu2O4 and GeOCuO2 to show the inert cationic and the active magnetic anionic cuprate complexes.
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[^21]: Here the indices are not dropped because c0 denotes also the calculated and cp the measured values.
[^22]: For 1 K ≤ T ≤ 4 K we observed a c0 ∝ T−1.8 law and a linear law for 0.35 K ≤ T ≤ 1 K. Its relative large Sommerfeld constant γ ≈ 90 mJ/(molK2) is noteworthy. The exponent 1.8 of the former range, being in between a 3D FM (3/2) and a quasi-2D Néel (2) state, resembles those of quasi-1D FM Cu-peptides (1.73 and 1.84) [20].
[^23]: In other chain cuprates with comparable or even smaller J-values but with α ∼ 1, considerably higher fields H ∼ 20-30 T are predicted to affect c0 in the para phase (aside from special effects caused by anisotropic terms in β).
For $\alpha=0.5$ and $N = 20$ $\chi(T)$ shows two maxima. In the plot the upper broad one is shown. The roughly estimated points 3 and 4 follow from Eq. (3) using the $J_1$, $T_m^\alpha$, $\Theta_{CW}$ reported [15], $r=0.5(0.9)$, and adopting $J_\perp/J_1 = \mp 0.2$ as well as $z_i = 1$ for the interchain interaction. However, with respect to mentioned uncertainties for Rb(Cs)$_2$Cu$_2$Mo$_3$O$_{12}$ they should be regarded as rough estimates.