Frustrated Cuprate Route from Antiferromagnetic to Ferromagnetic Spin-$\frac{1}{2}$ Heisenberg Chains: Li_2ZrCuO_4 as a Missing Link near the Quantum Critical Point

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From thermodynamics, local spin density approximation + Hubbard U studies and exact diagonalizations of a five-band Hubbard model on CuO_2 stripes we find that Li_2ZrCuO_4 (Li_2CuZrO_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 $\alpha = -J_2/J_1 \sim 0.3$ is close to the critical value $\alpha_c = \frac{1}{4}$. Comparing with related chain cuprates we explain the rather strong field dependence of c_p, the monotonic downshift of the peak of $\chi(T)$, and its increase for $\alpha \rightarrow \alpha_c + 0$.

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The one-dimensional (1D) spin-$\frac{1}{2}$ 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 $\chi(T)$ at $k_B T_m^{\chi} \approx 0.64J$ and of the specific heat $c_v(T)$ at $k_B T_m^{c} \approx 0.48J$, (ii) $c_v \propto T/J$ at $T \rightarrow 0$, and (iii) $\chi^*(0) = J\chi(0)/Ng^2\mu_B^2 = 1/\pi^2$ and $d\chi(T)/dT \rightarrow +\infty$ at $T \rightarrow 0$. Hereafter $J \equiv J_1$ denotes the nearest neighbor (NN) exchange. For ferromagnetic (FM) $J_1 < 0$, $\chi(T) \propto 1/T^2$ and $c_v \propto \sqrt{T/|J_1|}$ at $T \rightarrow 0$; c_v shows a broad maximum at $k_B T_m^{c_v} = 0.35|J_1|$ and a field induced 2nd maximum at low T and $H < 0.008|J_1|/g\mu_B$ [2]. The general Hamiltonian $\mathcal{H}$ with next-nearest neighbors (NNN) J_2 or further in-chain exchange J_i included

$$\mathcal{H} = \sum_i J_1 \mathbf{S}_i \mathbf{S}_{i+1} + J_2 \mathbf{S}_i \mathbf{S}_{i+2} + J_3 \mathbf{S}_i \mathbf{S}_{i+3} + \ldots, \quad (1)$$

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 $GeCuO_3$ [3]. 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 [5–7], and to helicoidal ground states found in some chain cuprates at low T [8–17]. However, issues such as the behavior at very low T and in magnetic fields near the critical point $\alpha_c = -J_2/J_1 = \frac{1}{4}$ 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 ϕ given by $\cos\phi = -J_1/4J_2 \equiv \frac{1}{4}\alpha^{-1}$. This helix interpolates between a FM chain at $0 \leq \alpha \leq \alpha_c$ and two decoupled AFM chains at $\alpha = \infty$. Noteworthy, α_c is unaffected by quantum effects [17]. Since this should hold for the case of long-range in-chain couplings, too, we expect a down(up)shift of α_c for AFM (FM) J_i, $(i \geq 3)$:

$$\alpha_c = \frac{0.25}{1 + 2.25\frac{J_3}{J_2} + 4\frac{J_4}{J_2} + 6.25\frac{J_5}{J_2} + 9\frac{J_6}{J_2} + \ldots}. \quad (2)$$

Recently, low $T - \chi(T)$ data for $Rb(Cs)_2Mo_3Cu_2O_{12}$ [15,16] have been refitted by the isotropic $J_1 - J_2$ HM near α_c. However, both compounds seem to be affected by Dzyaloshinskii-Moriya interactions $\mathbf{D}_{ij}(\mathbf{S}_i \times \mathbf{S}_j)$ [6] and exhibit a very complex crystal structure complicating a theoretical study even more.

Hence, studies of less complex systems described by Eq. (1) but with $|\alpha - \alpha_c| \ll 1$ are of general interest. Analyzing $\chi(T)$, $c_P(T, H)$, and the electronic structure of Li_2ZrCuO_4 we will show that it is a suitable candidate to probe the vicinity of α_c from the helical side. Together with data for related systems with $\alpha \geq 1$ it provides a so-far missing link near α_c to study, e.g., the α dependence of relations (i)–(iii), moving from AFM to FM chains.

The orthorhombic crystal structure of Li_2ZrCuO_4 [18] (space group Cccm) with the lattice constants $\mathbf{a} = 9.385$ Å, $\mathbf{b} = 5.895$ Å, $\mathbf{c} = 5.863$ 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

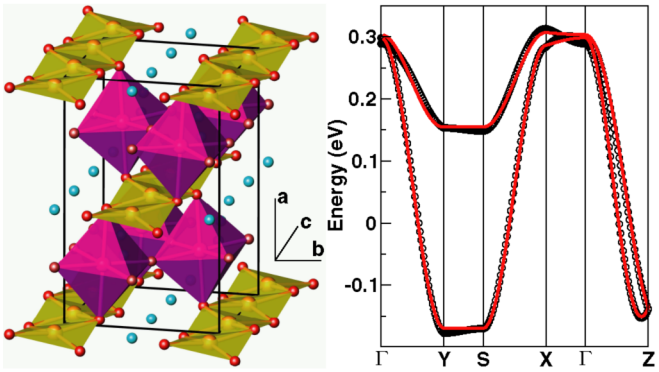

FIG. 1 (color online). Crystal and electronic structure near the Fermi level $E_F = 0$ of Li_2ZrCuO_4. Left: Crystal structure; nonplanar edge-shared CuO_2 chains run along c, separated by ZrO_6 octahedra and Li^+ ions [Li (split) positions near Zr are omitted for clarity]. Right: LDA-FPLO band structure (○) and TB fit (solid line).

of 2.002 Å and the Cu-O-Cu bond angle $\gamma = 94°$ resemble those with FM J_1.

The γ-polymorph of Li_2ZrCuO_4 (Li ordered) was prepared by a solid state reaction of Li_2CO_3, ZrO_2, and Cu-O [19]. 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_2ZrCuO_4 measured in a range $2 \le T \le 350$ K for 0.1 T by a quantum design SQUID magnetometer is shown in Fig. 2. From the observed $T_m^\chi \approx 7.6$ K one might at first glance expect an AFM spin liquid regime with J_1 or $J_2 \approx 12$ K, if γ 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 nonideal chain geometry or vice versa $J_2 \gg |J_1|$. But $\chi^*(T_m)$ is twice as large as the AFM-HM value of 0.1469 ($\chi(T_m) = 0.0183$ emu/mole for $g = 2$). $1/\chi(T) \propto T + \tilde{\Theta}_{CW}$ reveals a FM Curie-Weiss temperature $\tilde{\Theta}_{CW} = -24$ 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 the quantum design physical properties measurements system (see Fig. 3). It shows a relative sharp peak near 6.4 K at $H = 0$. Using $c_p \approx c_v$ [20], the observed ratio $T_m^\chi/T_m^{c_p} = 1.17$ differs from 1.33 predicted by the AFM-HM. Note that T_m^c nearly coincides with the T for which $d\chi(T)/dT$ becomes maxima. Hence, it is unclear whether this peak can be attributed either to a c_p anomaly indicating often a magnetic phase transition [21], or to a specific feature of the disordered phase generic for the 1D frustrated $J_1 - J_2$ HM at $\alpha_c < \alpha < 0.4$. Here c_v exhibits a *two-peak* structure [5–7]: a sharp peak at low T under consideration and a broad one at high T hidden in the phonon region ($k_B T \sim 0.65|J_1| \approx 260$ K in the present case). Anyway, with increasing field T_m^c is downshifted and $c_p(T_m)$ is suppressed but $c_p(T)$ increases rapidly for $T \ge 12$ K, well above a possible phase transition near 6 K.

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 $\Delta c(H) = c(H) - c(0)$ and $-\Delta T_m^c = T_m^c(0) - T_m^c(H) \propto H^2$ already at weak fields $H \le 9$ T results from the vicinity to α_c [23]. 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 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 ~363 K using the $\chi(T)$ data for $\alpha = 0.29$. The low-T peaks extrapolated to $N = \infty$ would be expected near $k_B T_m^c \approx 0.013(0.0115)|J_1|$, respectively, i.e., near 5.3(4.2) K below the observed one at 6.4 K, similarly as the expected $T_m^\chi \approx 4.5 \pm 1.7$ K is below the observed one near 7.6 K (Figs. 2–4). These observations

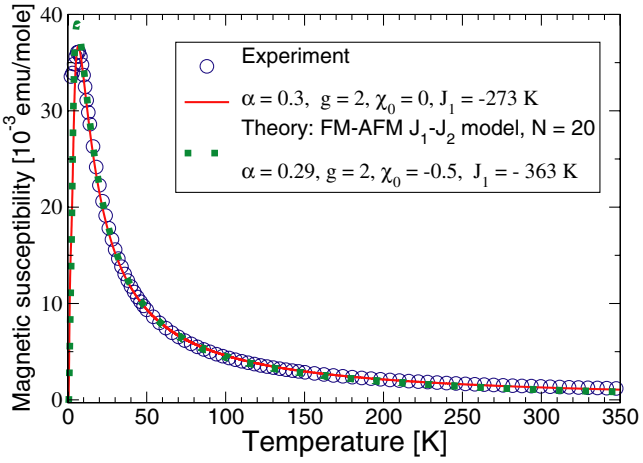

FIG. 2 (color online). Magnetic susceptibility of Li_2ZrCuO_4 together with fits by the $J_1 - J_2$ model for periodic chains.

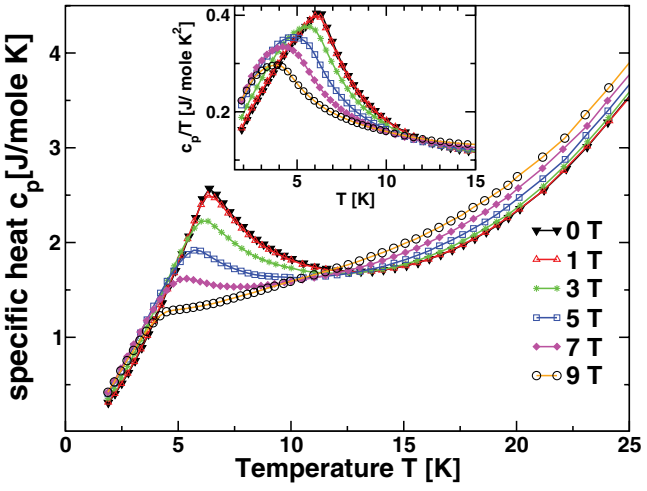

FIG. 3 (color online). Specific heat c_p of Li_2ZrCuO_4 vs T at various external magnetic fields H. Inset: the same for c_p/T.

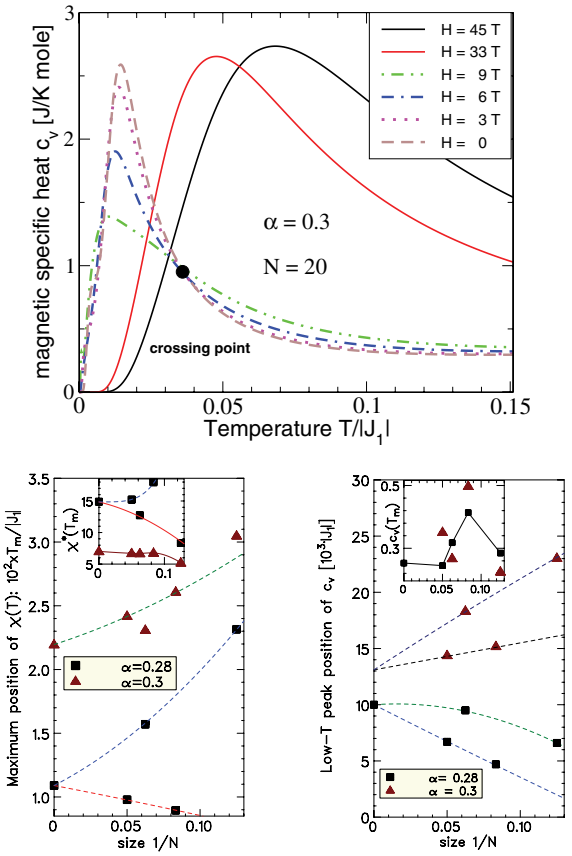

FIG. 4 (color online). Specific heat c_v vs temperature in units of $|J_1|$ for various magnetic fields H within the FM-AFM-$J_1 - J_2$ HM for $\alpha = -J_2/J_1 = 0.3$ and a ring with $N = 20$ sites (upper row). Finite size effects for the maximum of $\chi(T)$ (left) and the low-T maximum of $c_v(T)$ (right) (lower row). The $N = \infty$ values are taken from TMRG results of Ref. [6].

are in accord with the scenario of a phase transition at 6 K as discussed above. The slightly different results from fitting $\chi(T)$ or $c_p(H, T)$ might be due to anisotropies and interchain coupling.

To estimate the interchain coupling, we consider the measured Curie-Weiss temperature $\tilde{\Theta}_{\rm CW} = r\Theta_{\rm CW} = -24$ K, where $1 \geq r(T) \approx 0.25$ is estimated from the calculated $d\chi^{-1}(T)/dT$ taken at the highest available T. Here it is still outside the asymptotical CW range $k_B T \gg |J_1|$, where $r \to 1$. The high-T expansion of $\chi(T)$ yields $\Theta_{\rm CW} = 0.25 \sum_i z_i J_i$, i.e.,

$$2\tilde{\Theta}_{\rm CW}/r = J_1(1-\alpha) + J_3 + J_\perp + 2J_{d1} + 2J_{d2}, \quad (3)$$

where the neighbor number $z_i = 2$ for couplings along the c and b axes and $z_i = 4$ for diagonal interchain exchange ($d1$, $d2$) within the b, c plane. From the tight binding (TB) fit of the band dispersion we find similar direct and diagonal interchain transfer integrals $t_\perp \approx t_{d1} \approx t_{d2}$. Setting $J_\perp = J_{d1} = J_{d2}$, we found $|J_1|, J_2 \gg J_\perp \approx 9$ K in accord with the LDA results ($J_\perp \approx 7$ K). Thus, the adopted 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 correlation 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, version 5.00-19) [24]. 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 [25] we used $U_{3d} = 6.5 \pm 1.5$ eV and $J = 1$ eV for the intra-atomic exchange. Comparing total energy differences for different magnetic superstructures [26], we obtain $J_1 = -151 \mp 35$ K and $J_2 = 35 \mp 12$ K. Using a typical one-band Hubbard $U_{\rm eff} \approx 3.5$ eV as well as t_2 and t_3 from the TB fit of the band at E_F (Fig. 1) results in $J_2 = 46$ K and $J_3 = 6$ K employing $J_i = 4t_i^2/U$. Thus, we arrive close to $\alpha_c = 0.195$ in the present case of $J_3 \neq 0$ [see Eq. (2)].

Finally, a collection of known T_m^χ/J_2 and $\chi(T_m)$ values from other chain cuprates we derived from their $\chi(T)$ data [9–12,27], is shown in Fig. 5 [28]. In particular, it is clear why the large-α chains in $SrCuO_2$ and $LiVCuO_4$ are often regarded as AFM-HM archetypes [29]. Only after the discovery of spirals, detailed inelastic neutron scattering studies, and our three component theoretical analysis (HM, Cu-O Hubbard model, LDA) initial assignments for $LiVCuO_4$ and $LiCu_2O_2$ were corrected [8–11]. Similarly, among systems assigned so far as "perfect" realizations of the AFM/FM HM (e.g., [21,22]) could be further $J_1 - J_2$

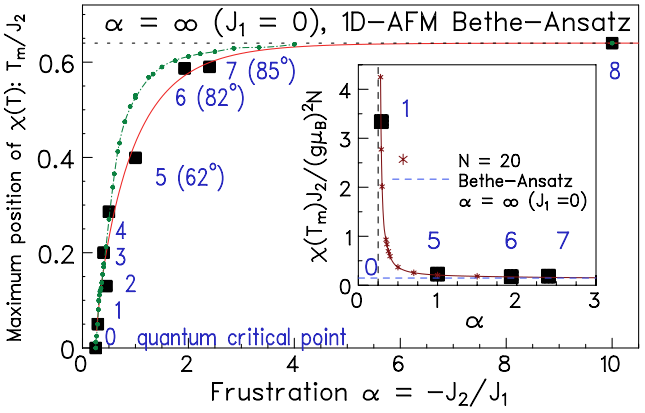

FIG. 5 (color online). Empirical T_m^χ in units of the fitted J_2 value of the FM-AFM $J_1 - J_2$ model for several frustrated chain cuprates (black squares). 0: $\alpha_c = \frac{1}{4}$; 1: Li_2ZrCuO_4; 2: $Pb_2[CuSO_4(OH)_2]$; 3: $Rb_2Cu_2Mo_3O_{12}$; 4: $Cs_2Cu_2Mo_3O_{12}$; 5: $LiCu_2O_2$; 6: $NaCu_2O_2$; 7: $LiVCuO_4$; and 8: $SrCuO_2$. The measured pitch is given in brackets. The small ○ denote the full diagonalization results of the $J_1 - J_2$ model on rings with $N = 20$ sites. Inset: the maximum value of $\chi(T)$.

candidates. Similar plots which accent the FM critical point can be made for the low-T peak of c_v or $\chi(0)$ (which monotonically increases and diverges finally as $\alpha \rightarrow \alpha_c$) [30]. We expect that a vanishing $T_m^{\chi(c)}$ and a diverging $\chi(T)$ for $T \rightarrow 0$ in approaching α_c are generic for a FM critical point. It should hold for models beyond the $J_1 - J_2$ HM. Further couplings do affect the helical phase in changing, e.g., the pitch and α_c [see Eq. (2)].

Comparing $\alpha \sim \alpha_c$ for Li_2ZrCuO_4 with $\alpha \gg \alpha_c$ we found for other chain cuprates the question arises, what is the microscopic reason for? There are at least two options: (i) an enhanced $|J_1|$ at a standard J_2 value and vice versa; (ii) a slightly enhanced $|J_1|$ at a reduced J_2. Case (i) can be ascribed to enhanced FM contributions to J_1 which arise from the direct exchange K_{pd} or from the Hund's rule coupling at the sharing O ions within a Cu $3d$ O $2p$ extended Hubbard model. Unfortunately, there is no generally accepted K_{pd} value, but it is the most sensitive quantity for the determination of J_1 in edge-shared cuprates [31]. Nevertheless, usually K_{pd} is treated as a fit parameter: The well-studied Li_2CuO_2 can be described with $K_{pd} = 50$ meV [32], whereas microscopic calculations for La_2CuO_4 yield 180 meV [33] and a structural analysis of $GeCuO_3$ was performed adopting $K_{pd} = 110$ meV [31]. Within the Cu $3d_{yz}$ O $2p_y, p_z$ extended Hubbard model for planar Cu_nO_{2n+1} open chains ($n \leq 5$), we adopted $K_{pd} = 70$ meV. From a direct mapping onto the $J_1 - J_2$ HM using $\Delta_{p_yd} = 2.5$ eV, $\Delta p_z d = 3.2$ eV, and Li_2CuO_2-like parameters, we found $J_1 = -317$ K, $J_2 = 90$ K, and $\alpha = 0.284$, close to our empirical values. In case (ii) supported by the LSDA + U results, we arrive also close to α_c. Here J_2 amounts 46 K, only. From a comparison with other cuprates in Fig. 5 more insight will be gained into the nature of the exchange and the FM critical point.

To conclude, we have shown that a growing number of edge-shared chain cuprates form a special family which thermodynamics can described within the $J_1 - J_2$ model with FM NN and AFM NNN exchange. Moving from the AFM-HM towards α_c, almost achieved for Li_2ZrCuO_4, observed monotonic changes can be explained. Only chains near the FM critical point show peculiar physical properties such as the strong H dependence of c_p in a large T range reported here. Further studies of Li_2ZrCuO_4 at very low T, under pressure, and in high fields are highly desirable. If the observed c_p 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 $LiCu_2O_2$ [8]. Inelastic neutron scattering studies might be helpful to refine the exchange integrals, especially with respect to the interchain coupling.

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