$Ca_2Y_2Cu_5O_{10}$: The First Frustrated Quasi-1D Ferromagnet Close to Criticality

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$Ca_2Y_2Cu_5O_{10}$ is built up from edge-shared CuO_4 plaquettes forming spin chains. From inelastic neutron scattering data we extract an in-chain nearest-neighbor exchange $J_1 \approx -170$ K and the frustrating next-neighbor $J_2 \approx 32$ K interactions, both significantly larger than previous estimates. The ratio $\alpha = |J_2/J_1| = 0.19 \pm 0.01$ places the system close to the critical point $\alpha_c = 0.25$ of the J_1-J_2 chain but in the 1D *ferromagnetic* regime. We establish that the vicinity to criticality only marginally affects the dispersion and coherence of the spin-wave-like magnetic excitations but instead results in a dramatic T dependence of high-energy Zhang-Rice singlet excitation intensities.

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Frustrated low-dimensional magnets serve as breeding grounds for novel and exotic quantum many-body effects. $Ca_2Y_2Cu_5O_{10}$ (CYCO) and the closely related Li_2CuO_2 (LCO) are considered candidates for this type of unconventional and challenging physics [1–3]. These systems belong to the rich class of frustrated edge-shared chain cuprates (ESC) and their magnetic excitation spectra, as probed by inelastic neutron scattering (INS), show striking puzzles. It was claimed that the dispersion of the magnetic excitations in CYCO shows an anomalous *double* branch [1] (see also Supplemental Material Fig. S1 [4]) while LCO exhibits a single but weakly dispersing branch [2]. Such observations would point at a strong deviation of the dispersion from standard linear spin wave theory (LSWT) in any realistic ESC parameter regime. This motivates one to look for and investigate scenarios with more sophisticated many-body physics, e.g., the presence of significant antiferromagnetic (AFM) interchain couplings (IC), causing the branch doubling in CYCO [1]. However, such a scenario invoking strong quantum effects [1,3] seems to be at odds with the observed large and almost saturated magnetic moments $\sim 0.9\mu_B$ at $T \ll T_N \approx 30$ K [5,6], which suggests rather *weak* quantum fluctuations.

To resolve the situation it is essential to identify the precise values of the exchange interactions in these ESCs, both within and between the spin chains. To this end, it is key to measure and at the same time calculate the elementary magnetic excitations, ideally for directions of momentum transfer in which the excitations depend most sensitively on the strength of the in-chain couplings. From scattering along the a axis of CYCO, which does *not* fulfill this condition, a moderate value of the ferromagnetic (FM) nearest-neighbor (NN) coupling $J_1 \approx -93$ K has been extracted [3] with a tiny frustrating AFM next-nearest-neighbor (NNN) exchange $J_2 \approx 4.7$ K (see Fig. 1). From a theoretical point of view this is rather unexpected for the ESC chain geometry due to the presence of sizable O-O $2p$ hopping along the chains. A recent reassessment of the exchange strengths based on INS on isotopically clean $^7Li_2CuO_2$ [7] has revealed a relatively large FM coupling $|J_1| > 200$ K, which is more than a factor of 2 greater than earlier theoretical estimates [8]. In CYCO, one would therefore expect a comparable large value of J_1 due to its structural similarity. In fact, high-T ^{89}Y NMR data on CYCO appear difficult to reconcile with small $|J_1|$ values [9]. Here we show that indeed by measuring with INS the magnetic excitations in CYCO along $\mathbf{Q} = (H, 0, 1.5)$, a direction where they are little affected by interchain couplings, one extracts a substantial in-chain $J_1 \approx -170$ K and a frustrating $J_2 \approx 32$ K, so that $\alpha = |J_2/J_1| \approx 0.19$.

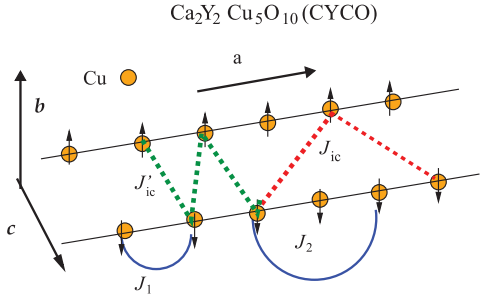

FIG. 1 (color). Schematic view of the structure of the CuO_2 chain layer and the main exchange paths of CYCO (see text).

This indicates an exceptional position of CYCO within the ESC family: close to the critical point of the J_1-J_2 model ($\alpha_c = 1/4$) but on the FM side of its phase diagram and in contrast with Li_2ZrCuO_4 ($\alpha = 0.3$ [10]) and LCO ($\alpha = 0.33$ [7], here the 3D spiral ground state is suppressed by small AFM IC like that shown in Fig. 1), both are in 1D on the *spiral* side of the critical point. We compare the obtained J values to a realistic five-band extended Hubbard pd model and L(S)DA + U calculations, which are in good agreement. The resulting magnetic excitations calculated with exact diagonalization compare well to the ones obtained with LSWT, implying that the coherence of the elementary spin-wave-like magnetic excitations is marginally affected by α and quantum fluctuations. However, the relatively large J_1 and α values obtained affect the thermodynamics [11]. The vicinity to the critical point set by $\varepsilon = \alpha - \alpha_c$ strongly affects both the magnitude and decreasing or increasing T dependence of the Zhang–Rice singlet (ZRS) excitation intensity for $\varepsilon > 0$ and $\varepsilon < 0$, respectively. This is manifest in resonant inelastic x-ray scattering (RIXS), EELS, and optics [12] measurements, as we will show.

CYCO has edge-shared CuO_2 chains along the a axis with the Cu^{2+} spins aligned FM along the a axis. The CuO_2 chains sit within the ac plane and alternate along the b axis with magnetically inactive cationic planes containing incommensurate and partially disordered CaY chains that produce a nonideal geometry in the CuO_2 chains (see Fig. 1). These mutual structural peculiarities might be responsible for the puzzling strong damping at large transferred neutron momenta [1,3], to be addressed elsewhere.

Our INS study at $T = 5.2$ K was performed with a fixed final neutron energy of 14.7 meV on a triple-axis neutron spectrometer TAS-2 installed at the JRR-3 by the Japan Atomic Energy Agency. Two directions, $\mathbf{Q} = (H, 0, 1.5)$, and $\mathbf{Q} = (H, 0, 1.25)$, were studied. To analyze the dispersion of the magnetic excitations we adopt the model given in Ref. [3]. Then, CYCO has the following main couplings $J(\mathbf{R})$, $\mathbf{R} \equiv (xa, yb, zc)$: NN and NNN couplings along the chain $J(1,0,0) \equiv J_1$, $J(2,0,0) \equiv J_2$, and the IC $J(0.5,0,0.5) \equiv J'_{\rm ic}$, $J(1.5,0,0.5) \equiv J_{\rm ic}$, $J(0,1,0) \equiv J_b = -0.06$ meV, and $J(0.5,0.5,0) \equiv J_{ab} = -0.03$ meV. For the small interplane FM couplings J_b and J_{ab}, we adopt the values from Ref. [3]. Their contribution to the in-chain dispersion is negligible. Within the LSWT, the dispersion of the magnetic excitations is given by Eq. (2) of Ref. [3]: $\omega^2(\mathbf{q}) = A_{\mathbf{q}}^2 - B_{\mathbf{q}}^2$, $A_{\mathbf{q}} \equiv J_{\mathbf{q}} - J_{\mathbf{0}} + \tilde{J}_{\mathbf{0}} - D$, $B_{\mathbf{q}} \equiv \tilde{J}_{\mathbf{q}}$, where $J_{\mathbf{q}} = (1/2)\sum_{\mathbf{r}} J_{\mathbf{r}} \exp(\imath \mathbf{q} \cdot \mathbf{r})$ is the Fourier transform of intrasublattice interactions and analogously for the intersublattice interactions $\tilde{J}_{\mathbf{q}}$. The dispersion along $(0, 0, L)$ shown in Fig. 3 (c) of Ref. [3] depends only on $J_s = J'_{\rm ic} + J_{\rm ic}$. Its value as well as the anisotropy parameter D may be found from the INS data for $\mathbf{q} = (0,0,1.5)$, $(0, 0, 1.25)$: $J_s^2 = \frac{1}{2}[\omega^2(0,0,1.5) - \omega^2(0,0,1.25)]$, $D = 2J_s - \omega(0,0,1.5)$. Using $\omega(0,0,1.5) = 5.03 \pm 0.03$ and $\omega(0,0,1.25) = 3.85 \pm 0.01$ meV, we obtain $J_s \approx 2.29$ meV and $D \approx -0.45$ meV [13], which is very close to $J_s = 2.24$ meV and $D = -0.26$ meV found in Ref. [3] (the different temperature $T = 7$ K of these measurements along $\mathbf{Q} = (H, 0, 0)$ might be responsible for slight deviations of our fit from the data, cf., Fig. 2). The dispersion along the line $(H, 0, 1.5)$ depends only on the in-chain J's (if the tiny interplane $J_{ab} = -0.03$ meV is ignored). It reads $\omega(\mathbf{q}) = A_{\mathbf{q}} = J_{\mathbf{q}} - J_{\mathbf{0}} + \omega(0, 0, 1.5)$. These J values can be accessed from the dispersion along this line with much higher precision than from the previously reported data along $(H, 0, 0)$, and we have [13]:

$$J_1 = -14.69 \pm 0.5(4\%) \text{ meV} \approx -170.4 \text{ K}, \quad (1)$$

$$J_2 = 2.78 \pm 0.2(7.6\%) \text{ meV} \approx 32.2 \text{ K}. \quad (2)$$

The dispersions along $(H, 0, 0)$ (reported in Ref. [3]) and $(H, 0, 1.25)$ (given here) are slightly affected by $J'_{\rm ic}$ and $J_{\rm ic}$; our fit gives $J'_{\rm ic}/J_{\rm ic} = \tau \approx 1.03 \pm 0.12$ (12%) at variance with $\tau = 2$ adopted in Ref. [3]. Our band-structure calculations suggest an even smaller value of $\tau \approx 4/9$. It might be refined empirically if one measures also along $(H_0 \neq 0, K, L)$ for any K value; e.g., for $H_0 = 1/6$, the dispersion depends solely on $J'_{\rm ic}$. With the aim to detect quantum effects beyond the LSWT, we calculated the dynamical structure factor $S(\omega, q)$ using exact diagonalizations (see Fig. 3).

In Fig. 2, the INS data together with the refined new LSWT fit are shown. $S(\omega, q)$ for our set and that of Ref. [1] are shown in Fig. 3. The peak positions always nicely follow the LSWT curves; however, our set gives a better description of the INS data than that in Ref. [3] (Fig. 4 therein) where the artificial double branching was ascribed to AFM IC. Indeed, it induces some intensity apart from the LSWT curve, but these intensities are far too weak to be

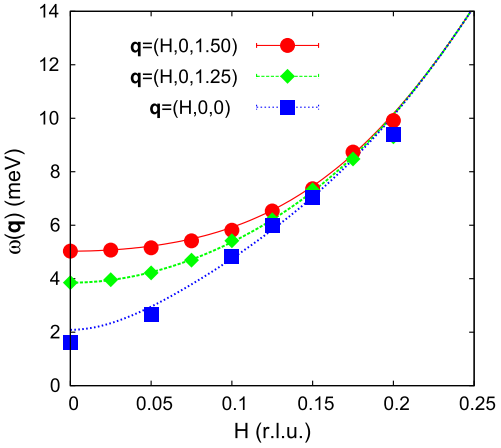

FIG. 2 (color online). Dispersion along three lines of the first Brillouin zone parallel to the a axis, obtained from constant $\mathbf{q}$ scans. The LSWT fit was refined only for the dispersion along $(H, 0, 1.5)$, and it is shown by thin lines.

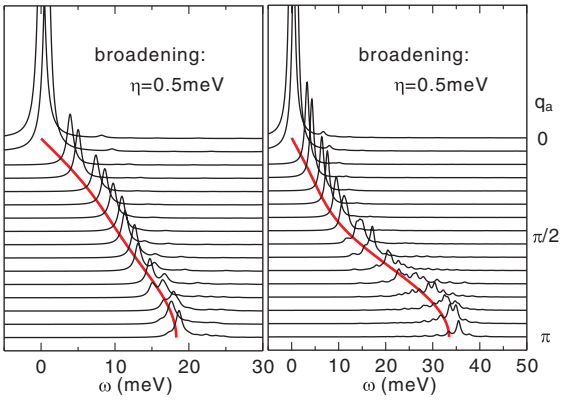

FIG. 3 (color). Magnetic dynamical structure factor $S(\omega, q_a)$, $\mathbf{q} \parallel \mathbf{a}$ for the J set of Ref. [1] (left) and for our set (right) from exact diagonalizations with $L = 14 \times 2$ and 15×2 adopting $D = 0$ for simplicity, $\tau = 2$ and $4/9$, respectively, and $J_s = 2.24$ meV (see Ref. [17]). Red lines (the curves just to the left of the peaks of the magnetic dynamical structure factor): dispersion from LSWT for both parameter sets (see Fig. 2 and text).

considered as a branch doubling. Notice the inflection point at $\pi/2$ for finite α. The total dispersion width is given solely by $2|J_1|$. The relatively large value of $|J_1|$ does not allow one to extract directly Θ_{CW} from a $1/\chi(T)$ plot using only data up to 300 K. Instead, a much broader T interval up to about 800 K would be required to reach the asymptotic high-T limit necessary for a proper quasilinear behavior. Alternatively, higher orders in the high-T expansion can be applied [14]. Hence, the reported AFM values of the Curie-Weiss temperature $\Theta_{\mathrm{CW}} \sim -15$ K [15] or weak FM ones $\Theta_{\mathrm{CW}} \sim +8$ K [16] are rather artificial. Using the J's from our INS fits, we predict instead a markedly larger FM value

$$\Theta_{\mathrm{CW}} = 0.5(|J_1| - J_2) - J'_{\mathrm{ic}} - J_{\mathrm{ic}} - J_{ab} = +43.4 \text{ K}. \quad (3)$$

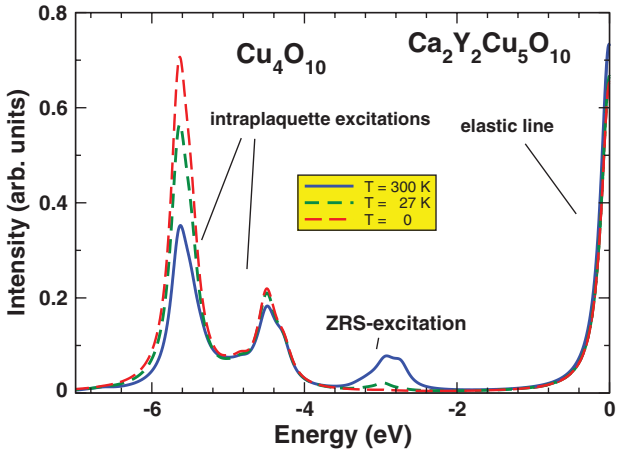

FIG. 4 (color). T-dependent O K RIXS spectrum for xx polarization from a Cu_4O_{10} cluster within exact diagonalization using a Lorentzian broadening (half width $\Gamma = 0.13$ eV).

Since we found $\alpha < \alpha_c$, we readily predict the value of the two-dimensional saturation field H_s which is here determined solely by the total AFM IC like that for LCO [17]: $gH_s = 4(J'_{\mathrm{ic}} + J_{\mathrm{ic}}) = \frac{2}{g}77.4\mathrm{T} \approx 64.8$ T, refining an estimate of 70 T for $H \parallel b$ and $g = 2.39$ from low-field magnetization data [16]. Next we consider the magnetic moment in the ordered state at low T. Within the LSWT, the reduction due to quantum fluctuations is about 6.8%, which yields $1.07\mu_{\mathrm{B}}$ to be compared with the experimental value of $0.92 \pm 0.08\mu_{\mathrm{B}}$ [6], which however is affected by the chemical reduction effect since about 0.22 ± 0.04 of the local moment resides on the O $2p$ orbitals.

The exchange coupling strengths can also be determined by DFT + U calculations. For this, we used the full potential scheme FPLO [18] (versus fplo9.01) and performed supercell calculations for different collinear spin arrangements applying local density approximation and generalized gradient approximation functionals [19,20]. The Coulomb repulsion U_{3d} was varied in the physical relevant range from 5 to 8 eV for a fixed $J_{3d} = 1$ eV. In our calculations, the incommensurate crystal structure of CYCO can be treated only approximatively. Thus, we neglect (i) the modulation of the Cu-O distances within the CuO_2 chains and its buckling and (ii) the incommensurability of the CuO_2 and the CaY subsystems. In particular, the CuO_2 chains were treated as ideal planar chains reflecting an averaged Cu-O distance of 1.92 Å and a Cu-O-Cu bond angle of 94.5°. Furthermore, we modeled the CaY layer by a Na layer to preserve the half filling of the system. The structure of the simplified model systems is given in the Supplemental Material [4]. These structural simplifications allow a reliable modeling of J_1 yielding an FM value ~ -150 K (see Supplemental Material [4]). In previous studies of (i) chain buckling and (ii) cation-related crystal field effects for closely related ESC [21,22], it was shown that J_1 is rather robust whereas J_2 is strongly reduced by a factor of 2 to 3. Thus, our $-J_1 \sim 150$ K is considered a rather reliable lower estimate by about 10 to 20% with respect to the buckled chain geometry in CYCO. However, in view of the drastic dependence of J_2 on these parameters [21,22], a derivation of a reliable value from the applied model structure is difficult.

Our results show that CYCO fits the general experience of a sizable FM J_1 value for ESC in contrast to the assignments of only a few K, proposed for $LiVCuO_4$ [23] and $NaCu_2O_2$ [24]. Such small J_1 values would put them in a region of strong quantum fluctuations, harboring the difficulty that the observed pitch angle cannot be described classically [25]. Whereas the vicinity of CYCO to the quantum critical point only weakly affects the dispersion and coherence of the elementary, spin-wave-like magnetic excitations, we will show that the amplitude to excite Zhang–Rice singlets at typical high energies probed by spectroscopic means depends strongly on the frustrating J_2 and temperature. To do so, we here performed exact

diagonalization calculations using an extended five-band Cu $3d$ O $2p$ Hubbard model for CYCO with a standard parameters [26]. To fit the INS-derived value of $J_2 = 32$ K, $t_{px,px} = 0.59$ eV has been slightly reduced as compared with LCO (0.84 eV, $J_2 = 76$ to 6 K), which probably simulates the deviations from the ideal chain geometry. Mapping the spin states of the five-band Hubbard model onto a frustrated spin model, we obtain $J_1 = -177.5$ K and $J_2 = 32.3$ K in full accord with the LSWT analysis of the INS data given above. We stress that the value of J_1 is mainly determined by the direct FM exchange coupling $K_{pd} = 65$ meV and not by the Hund's rule coupling on the O sites $J_p = 0.5(U_p - U_{p_x p_y}) = 0.6$ eV as often adopted. The significant value of J_1 is generic for ESC with a Cu-O-Cu bond angle $\varphi < 96°$ at variance from the case of $CuGeO_3$ with $\varphi \approx 98°$, causing an AFM J_1.

As a modern spectroscopy, RIXS provides valuable insights into the correlated orbital and electronic structure (for a review see Ref. [27]). Therefore, we also studied the T-dependent O K edge RIXS spectra for a Cu_4O_{10} cluster within exact diagonalization (see Fig. 4). We find a strong decrease of the intensity for the ZRS excitons with decreasing T, which is qualitatively in accord with general considerations for EELS and optics [12]. The not-yet-assigned feature observed for CYCO at 300 K near 527 eV (Fig. 5 in Ref. [28], counted from the 530 eV excitation energy) corresponds just to these excitations. It perfectly agrees with 2.95 eV obtained here. Notice that when one sets $t_{px,px} = 0$, thereby strongly suppressing $J_2 \propto t^2_{px,px}$, no ZRS exciton is observed even at 300 K. Hence, the frustrated FM differs qualitatively from a pure unfrustrated FM in its high-energy response.

To summarize, we have shown that $Ca_2Y_2Cu_5O_{10}$ is a frustrated quasi-1D ferromagnet close to criticality. This edge-sharing spin-chain compound has pronounced FM correlations in the presence of a sizable in-chain frustration. The main intensity of magnetic excitations in $S(\omega, q)$ is reasonably well-described within LSWT. The signatures of the sizable in-chain frustration found here cause (i) a characteristic curvature of the in-chain dispersion of magnetic excitations and (ii) Zhang–Rice singlet features at $\sim$3 eV that are strongly T-dependent and are detectable by spectroscopies. The antiparallel orientation between the spins of adjacent chains ordered ferromagnetically along the a axis below T_N is supported by a specific AFM interchain coupling that solely determines the saturation field. It causes interesting quantum effects that go beyond a linear spin wave description. These effects and the interplay of $J'_{\rm ic}$ and $J_{\rm ic}$ provide an interesting problem not yet investigated in full detail. However, such quantum effects are neither strong enough to cause a breakdown of LSWT nor strong enough to induce an additional branch of magnetic excitations, as suggested previously. Our results can further aid in the correct assignment of the frustration [23,24] in other ESC, including multiferroics, but especially for the complex chain-ladder system (La, Sr, Ca)$_{14}$Cu$_{24}$O$_{41}$ [29], which also possibly contains frustrated FM CuO_2 chains as suggested by their edge-sharing geometry and sizable NNN transfer integrals [30], giving rise to significant AFM J_2's. Their nonideal chains, as with CYCO, challenge one to look for more sophisticated but yet solvable theoretical models that include incommensurate and disorder effects.

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