Competition between Helimagnetism and Commensurate Quantum Spin Correlations in $LiCu_2O_2$

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Neutron diffraction and bulk measurements are used to determine the nature of the low-temperature ordered state in $LiCu_2O_2$, a $S = 1/2$ spin-chain compound with competing interactions. The spin structure is found to be helimagnetic, with a propagation vector $(0.5, \zeta, 0)$, $\zeta = 0.174$. The nearest-neighbor exchange constant and frustration ratio are estimated to be $J_1 = 5.8$ meV and $J_2/J_1 = 0.29$, respectively. For idealized quantum spin chains, these parameter values would signify a gapped spin-liquid ground state with commensurate spin correlations. The observed temperature dependence of the magnetic propagation vector in $LiCu_2O_2$ is attributed to a competition between incommensurate helimagnetism in the classical spin model and commensurability in the quantum case. It is also proposed that long-range ordering in $LiCu_2O_2$ is facilitated by intrinsic nonstoichiometry.

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A great deal of attention in magnetism has been recently given to systems with strong geometric frustration [1]. In classical magnets such competing interactions often result in helimagnetic ground states with incommensurate long-range order [2]. For quantum systems, a strong frustration can destroy long-range order altogether, producing gapped spin-liquid phases and other exotic states with only local spin correlations. Contrary to intuition, the periods and symmetries of such short-range correlations are often totally different from those in classical versions of the same models. Consider the simplest of frustrated magnets, namely, a spin chain with competing nearest-neighbor (NN) J_1 and next-nearest-neighbor (NNN) J_2 antiferromagnetic (AF) interactions. For a $\alpha = J_2/J_1 > 1/4$, the classical model has a spin-spiral structure with an *incommensurate* propagation vector $q = \arccos(1/4\alpha)$. In contrast, for the frustration parameter in the range $\alpha_c \approx 0.24 < \alpha < 0.5$, the quantum $S = 1/2$ model is a gapped spin liquid [3] with the correlation function peaked at a *commensurate* $q = \pi$ [4]. 3D interactions in real quasi-1D materials tend to suppress quantum spin fluctuations and restore semiclassical behavior. Frustrated quasi-1D systems thus become stage to a unique *competition* between classical incommensurate and quantum commensurate correlations.

Until now, this phenomenon has not been addressed experimentally, and the behavior of quasi-1D systems with competing quantum and classical periodicities remains largely unknown. Only a handful of frustrated-chain compounds have been identified, including $SrCuO_2$ [5], $N_2H_5CuCl_3$ [6], and Cu[2-(2-aminomethyl)pyridine] [7]. For the former two systems $\alpha \gg 1$, while for the latter $\alpha \approx 0.2 < \alpha_c$. The corresponding quantum and classical models both have incommensurate or commensurate spin correlations, respectively, and the competition phenomenon does not occur. Recent studies hint that the new quasi-one-dimensional charge-ordered material $LiCu_2O_2$ [8–12] contains $S = 1/2$ spin chains with α in the range $\alpha_c < \alpha < 0.5$, and thus may be an ideal model system for this investigation. The compound seems to possess characteristics of a spin-liquid state, including a gap $\Delta \approx 6$ meV in the magnetic excitation spectrum [11], and yet undergoes at least one magnetic ordering transition at $T_c \approx 22$ K [8,11,12]. To complicate matters, muon spin resonance studies indicate a precursor transition at $T_1 = 24$ K, and recent bulk measurements [11] point to yet another magnetic phase transition at $T^* = 9$ K. In the present work, we use neutron diffraction and additional bulk measurements to make sense of this complex behavior. We find concrete evidence of competing quantum and classical periodicities in $LiCu_2O_2$, and also discuss the important role of intrinsic *chemical* disorder.

As discussed in detail in Refs. [11,12], $LiCu_2O_2$ contains an equal number of Cu^+ and Cu^{2+} ions in distinct nonequivalent crystallographic positions. The magnetic Cu^{2+} ions carry $S = 1/2$ and form "triangular" two-leg ladders (Fig. 1), which can also be viewed as zigzag chains with competing NN and NNN interactions, J_{NN} and J_{NNN}, respectively. These chains run along the b axis of the orthorhombic crystal structure, and are well separated from each other by double chains of nonmagnetic Li^+ ions and layers of nonmagnetic Cu^+ sites. One key element of the present work was the preparation of samples with a thoroughly controlled chemical composition. Single crystals of $LiCu_2O_2$ were grown in an alundum crucible in air atmosphere using the self-flux method. The lattice parameters $a = 5.730(1)$, $b = 2.8606(4)$, and $c = 12.417(2)$ Å were verified by powder x-ray diffraction, which also confirmed the absence of any appreciable amounts of crystalline impurity phases. All crystals were found to be microscopically twinned with respect to the [1,1,0] plane, so that $a \approx 2b$ [12].

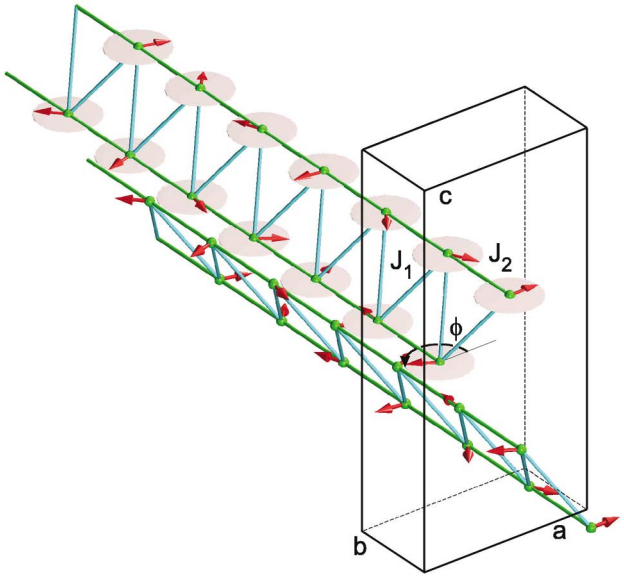

FIG. 1 (color). Crystallographic unit cell of $LiCu_2O_2$ showing the magnetic Cu^{2+} sites (green balls) and the planar helimagnetic spin structure (arrows) determined in this work.

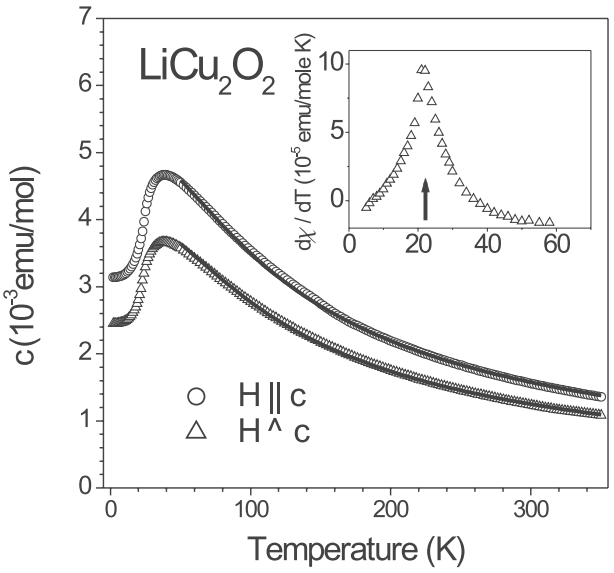

FIG. 2. Temperature dependence of magnetic susceptibility of $LiCu_2O_2$ measured in a magnetic field $H = 100$ Oe (symbols). The solid line is a fit based on the frustrated $S = 1/2$ chain model, as described in the text. Taking a numerical derivative (inset) reveals a phase transition $T_c = 22$ K (arrow).

Unexpectedly, a thermogravimetric analysis revealed that the samples had lower content of Cu^+ ions than follows from the stoichiometric formula $Li_1 + Cu_2 + O_2$. The density was determined to be $\rho = 5.12$ g/cm^3 at room temperature, which corresponds to an actual composition $Li_{1.16}Cu_{1.84}O_{2.01}$. Chemical disorder and a Cu deficiency by as much as $x = 16\%$ are thus inherently present. The "surplus" Li^+ ions in $Li_{1.16}Cu_{1.84}O_{2.01}$ occupy Cu^{2+} sites, due to a good match of ionic radii. Charge compensation requires that the introduction of 16% nonmagnetic Li^+ ions into the double chains is accompanied by a transfer of 16% of the $S = 1/2$-carrying Cu^{2+} ions onto the Cu^+ interchain sites. Thus, our $Li_{1.16}Cu_{1.84}O_{2.01}$ crystals (referred to as simply $LiCu_2O_2$ throughout the rest of the paper) have appreciable concentrations of both *nonmagnetic* Li^+ impurities in the zigzag chains, and *magnetic* Cu^{2+} impurities positioned in between chains.

The single-crystal samples were characterized using bulk techniques. $\chi(T)$ data were taken in a commercial SQUID magnetometer in the temperature range 5–350 K and a magnetic field $H = 100$ Oe applied parallel ($\chi_\parallel$) or perpendicular ($\chi_\perp$) to the (a, b) cleavage plane (Fig. 2). The main feature is a broad maximum at $T \approx 36$ K characteristic of a quasi-one-dimensional magnet, which signifies the formation of short-range correlations within the chains. Taking the temperature derivative of the magnetic susceptibility (Fig. 2, inset) reveals a sharp anomaly at $T_c = 22$ K, which we attribute to the onset of long-range magnetic order. The high-temperature part of the $\chi(T)$ curve is expected to be representative of isolated zigzag chains. The data taken above $T = 50$ K were therefore analyzed in the framework of the quantum $S = 1/2$ frustrated-chain model for which only the high-temperature expansions valid at $T \gtrsim J$ have been calculated to date [13]. The gyromagnetic ratios $g_\parallel = 2.04$ and $g_\perp = 2.23$ were measured in a separate electron spin resonance experiment. The frustration ratio was fixed at the value $\alpha = 0.29$, as determined from neutron scattering experiments (see below). With these assumptions excellent fits are obtained with $J_1 = 5.8(1)$ meV, as shown in solid lines in Fig. 2.

The anomaly at T_c is also manifest in the specific heat data measured using a "Termis" quasiadiabatic microcalorimeter and plotted in Fig. 3. The peak observed at $T \approx T_c$ is well defined, but, as indicated by arrows in the blowup plot, actually has a characteristic flattop that extends between $T_c = 22$ and $T_1 = 24$ K, in agreement with the results of Ref. [12]. The solid line in Fig. 3 represents a crude estimate for the phonon contribution. The temperature dependence of magnetic entropy is plotted in the lower right inset of Fig. 3. Characteristic of a low-dimensional system, a large fraction of the entropy is released above the ordering temperature. The sharp 9 K anomaly reported in Ref. [11] is totally absent in our $\chi(T)$ and $C(T)$ data. We suspect that this feature is due to an impurity phase, most likely Li_2CuO_2, which is known to go through an AF transition at 9 K [14].

The nature of the magnetically ordered state was determined in a neutron diffraction experiment using a single-crystal sample prepared with a naturally occurring Li isotope mixture and cut to a thin-plate $0.9 \times 15 \times 15$ mm^3 parallel to the (a, b) plane. The measurements were performed at the HB1 and HB1A 3-axis

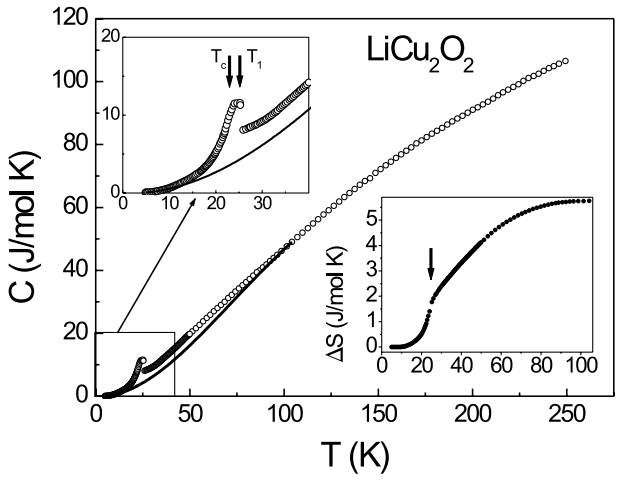

FIG. 3. The measured temperature dependence of specific heat in $LiCu_2O_2$ (open symbols) indicates a phase transition at $T_c \approx 22$ K and a possible precursor at $T_1 \approx 24$ K (arrows). Subtracting the phonon contribution (solid line) allows one to extract the temperature dependence of magnetic entropy (lower right inset).

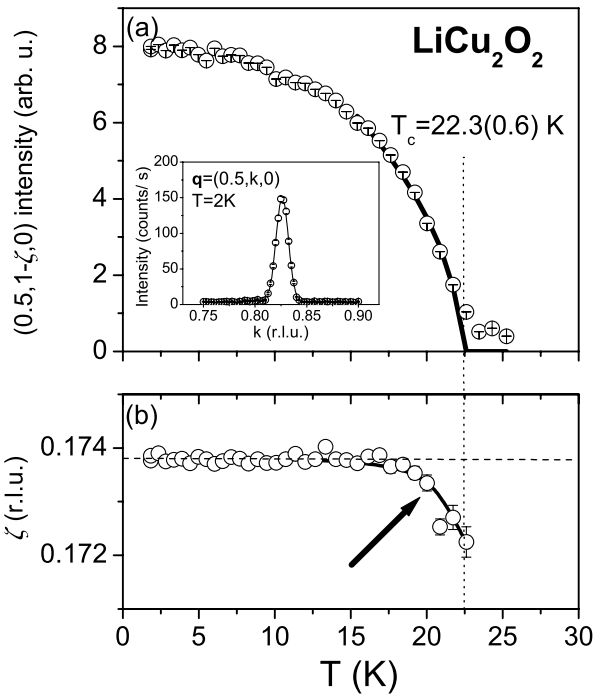

FIG. 4. (a) Measured temperature dependence of the (0.5, 0.826, 0) magnetic peak intensity in $LiCu_2O_2$ (symbols). The solid line is a power law fit to the data. Inset: k scan across this reflection measured at $T = 2$ K. (b) Measured incommensurability parameter ζ plotted as a function of temperature. The solid line is a guide for the eye. The arrow indicates the strong variation of ζ near T_c.

spectrometers installed at the High Flux Isotope Reactor at ORNL. Integrated Bragg intensities were collected in 2-axis mode, with a well-collimated incident neutron beam of a fixed energy $E_i = 14.7$ meV produced by a pyrolitic graphite PG(002) monochromator. Absorption corrections were applied assuming a thin-plate geometry. Additional high-resolution measurements of the magnetic propagation vector were performed in 3-axis mode, with a PG(002) analyzer and $48' - 40' - 40' - 240'$ collimators.

The main finding of this work is that below $T_c \approx 22$ K $LiCu_2O_2$ acquires *incommensurate* magnetic long-range order. The phase transition leads to the appearance of new Bragg reflections that can be indexed as $\{[(2n + 1)/2], k \pm \zeta, l\}$, n, k, l integer, $\zeta \approx 0.174$. Such peaks were observed in both crystallographic twins. The peak widths were found to be resolution limited along all three crystallographic directions at all temperatures below T_c. A typical scan across the (0.5, 0.826, 0) reflection taken at $T = 2$ K is shown in the inset of Fig. 4(a). The corresponding peak intensity is plotted as a function of temperature in Fig. 4(a). A simple power law fit to the data taken above $T = 15$ K yields $T_c = 22.3(6)$ K and $\beta = 0.25(0.07)$. The residual intensity seen in Fig. 4(a) at $T > T_c$ is due to critical scattering and is not a sharp peak in q space.

Interestingly, the magnetic propagation vector in $LiCu_2O_2$ is temperature dependent, as was deduced from Gaussian fits to k scans across the (0.5, 0.826, 0) peak [Fig. 4(b), symbols]. Below $T \approx 17$ K, the incommensurability parameter shows little variation and appears to have a strictly incommensurate value $\zeta = 0.1738(2)$. However, as T_c is approached from below, ζ progressively decreases as indicated by the arrow in Fig. 4(b). The minimum value of ζ observed in our experiments is about 0.172. Intensity being the limiting factor, we were unable to locate any magnetic Bragg reflections in the narrow temperature range $T_c < T < T_1$, though several reciprocal-space planes were thoroughly searched.

The spin arrangement in the ordered state was deduced from the analysis of 23 nonequivalent magnetic Bragg peaks with $0 \leq h \leq 3.5$, $0 \leq k \leq 1.5$, and $0 \leq l \leq 8$. A representational analysis of the crystallographic space group with the observed propagation vector [15] shows that, assuming all the magnetic Cu^{2+} sites carry the same moment (no spin-density wave), the symmetry-compatible magnetic structures are composed of uniform planar spin helixes propagating along the double zigzag chains. The fixed relative rotation angle between consecutive spins is $\phi = \pi(1 - \zeta)$. Any spins related by a translation along the c axis and a axes are parallel and antiparallel to each other, respectively. The orientation of the spin-rotation plane and an overall intensity scaling factor were refined using a combined reverse Monte Carlo and least squares algorithm to best fit the experimental data. An excellent fit is obtained with all spins confined to the (a, b) crystallographic plane, as visualized in Fig. 1. The relative phases of the spin spirals in the two zigzag chains in each crystallographic unit cell cannot be

determined due to the presence of q domains. Apart from that, the determination of the magnetic structure is unambiguous, as are our estimates for the coupling parameters of the proposed model. In an alternative model recently discussed in Ref. [16], frustration occurs within individual (rather then double) chains, which can, in principle, also produce the observed magnetic structure. However, the estimated coupling constants are incompatible with the observed magnetic propagation vector, and imply an unlikely dominance of NNN Cu-Cu interactions that span over large 5.7 Å distances.

In $LiCu_2O_2$, the competition between commensurate quantum spin fluctuations and the classical tendency to form an incommensurate helimagnetic state is rather severe. In the ordered phase, ζ is determined by the balance of exchange energies, which enables us to directly estimate the frustration ratio $\alpha = 1/4\cos(\pi\zeta) = 0.29$. As previously mentioned, an *isolated* zigzag chain with such α is *gapped* and has the nonuniform susceptibility $\chi(q)$ peaking at the commensurate AF position $q = 2\pi/b$. Magnetic ordering of weakly interacting gapped spin chains is commonly described by the chain-mean field (chain-MF) model. For $LiCu_2O_2$, one could expect this approach to work particularly well, as our data clearly show the dominance of 1D interactions in this material. However, in the chain-MF framework the projection of the magnetic propagation vector onto the chain axis corresponds to the maximum of bare chain susceptibility, i.e., to $\zeta = 0$. Such behavior is in stark contrast to the one actually observed in $LiCu_2O_2$, where helimagnetism ultimately wins at low temperatures and $\zeta > 0$.

A competition between commensurate and incommensurate ground states may be behind the observed T dependence of ζ, which increases as one goes deeper into the ordered phase. This temperature variation may, in turn, be responsible for one or more "devil's staircase" lock-in transitions, occurring in the narrow range $T_c < T < T_1$. A series of such transitions, smeared out by pinning and quenched disorder, and resulting in glassy states with short-range order, could very well account for the unusual phase found in this T range and characterized by a plateau in the measured $C(T)$ curve.

An important point to emphasize is that interchain interactions, which are ultimately responsible for long-range ordering in $LiCu_2O_2$, should be strongly influenced by the chemical disorder *inherently present in our samples*. In particular, they may be mediated by the estimated 16% of magnetic Cu^{2+} impurities positioned in between the chains. A similar model is realized in $(R_xY_{1-x})_2BaNiO_5$ rare earth nickelates, where classical R^{3+} ions bridge the Ni-based gapped spin chains [17]. Despite the gap in isolated chains, long-range order occurs for an arbitrary small concentration of impurities [18], and involves ordering of *both* the impurity spins and the chain spins. At the present stage, it is difficult to speculate about the implications of such a mechanism for $LiCu_2O_2$. Further work is also needed to understand the effect of a reduced correlation length in the chains themselves, due to nonmagnetic Li^{2+} impurities.

By mapping out the spin excitation spectrum, future inelastic neutron experiments will undoubtedly explain the apparent failure of the chain-MF approach in $LiCu_2O_2$ and further our understanding of this unique borderline quantum/classical frustrated and disordered antiferromagnet.

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