Dimer liquid state in the quantum antiferromagnet compound $LiCu_2O_2$

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Results of systematic structural, magnetic, electron-spin resonance, and specific-heat investigations of the $S=1/2$ quantum antiferromagnet compound $LiCu_2O_2$ are presented. A spin-singlet ground state is revealed at temperatures above $T\sim 23$ K. In this temperature region $LiCu_2O_2$ may be regarded as a quantum $S=1/2$ chain with competing nearest- and next-nearest-neighbor interactions in the intermediate range of the J_2/J_1 ratio ($\alpha_{c1}<J_2/J_1<\alpha_{c2}$). The size of the energy gap between the spin-singlet ground state and the first excited triplet, Δ, is found to be $\sim$72 K. The study confirms a magnetic phase transition in $LiCu_2O_2$, which results in the collapse of the spin-singlet ground state at a temperature below 23 K. In addition, a second low-temperature transition was found at $T\sim 9$ K. Peculiarities of the magnetic excitation spectrum in the dimer phase of $LiCu_2O_2$ and its magnetic structure are discussed.

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Recently, a considerable amount of attention has been given to theoretical and experimental investigations of low-dimensional (low-D) frustrated spin systems. This interest has been stimulated by theoretical predictions of a rich phase diagram and novel magnetic properties, which originate from the intensive interplay of geometrical frustration and quantum fluctuations in low dimensions. Quantum $S=1/2$ chains with competing nearest- and next-nearest-neighbor interactions have been intensively studied. The model Hamiltonian for these systems may be written in the form

$$H=\sum_i [J_1(S_i^xS_{i+1}^x+S_i^yS_{i+1}^y+\Delta_1S_i^zS_{i+1}^z) + J_2(S_i^xS_{i+2}^x+S_i^yS_{i+2}^y+\Delta_2S_i^zS_{i+2}^z)], \quad (1)$$

where S_i is the spin-S operator at site i, Δ_1 and Δ_2 are the exchange anisotropies, and J_1 and J_2 are the nearest- and next-nearest-neighbor interactions, respectively. Depending on the ratio between J_1 and J_2, this class of materials may exhibit a gapless collinear phase ($J_2/J_1<\alpha_{c1}$), a gapped disordered dimer liquid phase ($\alpha_{c1}<J_2/J_1<\alpha_{c2}$), or a quasi-long-range order spiral phase ($J_2/J_1>\alpha_{c2}$). The critical value α_{c1} runs from $\sim$0.33 in the XY case[1] to $\sim$0.2411 in the fully isotropic Heisenberg chain model.[2] The critical value α_{c2} increases from $\sim$1.26 in the XY case[3] to about of 1.8 in the isotropic Heisenberg chain case.[4] The presence of a sufficiently large exchange anisotropy ($|\Delta|>1$) may cause antiferromagnetic or ferromagnetic long-range spin correlations. Magnetic properties of the quantum $S=1/2$ dimerized frustrated chains can be significantly changed by introducing alternating exchange parameters.[5,6] One of the most challenging goals in these studies is to experimentally prove the rich variety of magnetic properties in the low-D quantum chain systems predicted theoretically.

$LiCu_2O_2$ is a mixed-valent compound with copper ions in the Cu^{2+} and Cu^{1+} oxidation states.[7,8] The crystallographic analysis of $LiCu_2O_2$ reveals a double-chain structure, with chains of Cu^{2+} ions propagating along the b axis. The low-D character of $LiCu_2O_2$ has been confirmed by magnetic susceptibility measurements, but the nature of the ground state in the low-D phase remains unclear. At $T\sim 23$ K the susceptibility shows a transition into a long-range-ordered phase.[9–11] This transition overshadows low-temperature features of the magnetic susceptibility, which would arise from the low-dimensional character of the system in the absence of the long-range order in AFM correlations and which are of special importance for investigation of the ground state in low-D systems. Electron-spin resonance (ESR) is an extremely powerful tool for investigating of the elementary excitation spectrum in solids. It provides direct information about the nature of the ground state, the type of magnetic structure, and allows one to determine phenomenological constants and magnetic parameters of magnetic materials. The main motivation of this work is to determine the nature of the ground state of $LiCu_2O_2$ and characterize its magnetic, resonance, and thermodynamic properties in the low-D phase.

$LiCu_2O_2$ has an orthorhombic crystal structure with a $Pmna$ space group [Fig. 1(a)]. The lattice constants at room temperature are $a=5.72$ Å, $b=2.86$ Å, and $c=12.4$ Å.[7,8] There are two linear Cu^{2+} chains, which propagate along the b axis and form a zigzag ladderlike structure [Fig. 1(b)]. The ladders are isolated from each other by both Li ions and the layers of nonmagnetic Cu^{+} ions. The distance between the magnetic next-nearest-neighbor Cu^{2+} ions (along the ladder) is about of 2.86 Å, and between the nearest-neighbor Cu^{2+} ions (that is, the length of the rungs) is about of 3.38 Å and 3.08 Å. Due to the slight difference in distance between the nearest-neighbor Cu^{2+} ions, an alternating term, $J_1+(-1)^i\delta$, should be considered in the Eq. (1). The distance between the Cu^{2+} ions from the neighboring ladders is 4.79 Å. The distance between the ladders along the a-axis direction (along which a possible super-exchange Cu^{2+}-Cu^{2+} coupling via oxygen bridges and, thus, some additional frustrations might be expected) is 5.72 Å. This distance is almost twice as large as the distance between

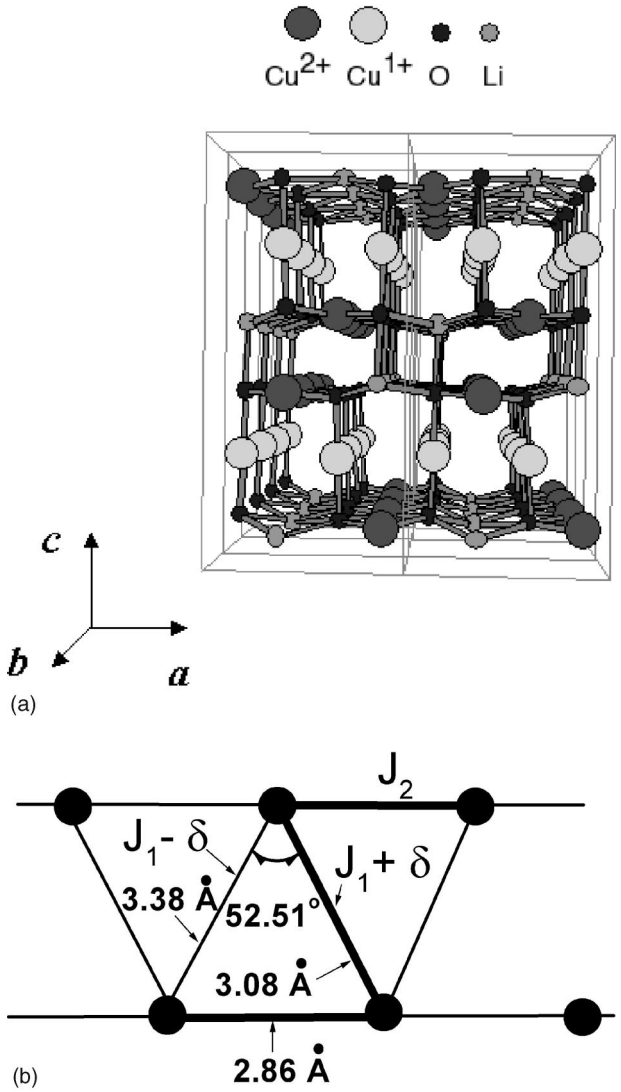

FIG. 1. (a) The crystal structure of $LiCu_2O_2$. The Cu^{2+} ion chains propagate along the *b* axis. (b) The schematic view of the double-chain structure of $LiCu_2O_2$ showing exchange pathways and distances between the Cu^{2+} ions.

Cu^{2+} ions along the ladders. Thus, the nature of the crystal structure facilitates a possible occurrence of the $S=1/2$ chain with competing nearest- and next-nearest-neighbor interactions and an alternating nearest-neighbor exchange interaction (asymmetric zigzag spin ladder).

$LiCu_2O_2$ crystals were grown using a self-flux method. A nonstoichiometric mixture of Li_2CO_3 and CuO was fired at 1250 °C for 4 h and then slowly cooled at a rate of 4 °C/h to 950 °C. Before proceeding with the ESR experiment a detailed microstructural analysis of the samples was performed using transmission electron microscopy (TEM). It revealed that the bulk material of the crystal is clearly the single-crystalline $LiCu_2O_2$ phase with an orthorhombic crystal structure. The crystal structure is twinned at the microscopic level in the *ab* plane. There is a second, LiCuO-impurity phase in the form of platelets with the dimension of $\sim 100 \times 7 \times 100$ nm^3 dispersed almost regularly inside $LiCu_2O_2$ [Fig. 2(a)]. This phase has copper ions in the Cu^{+} oxidation

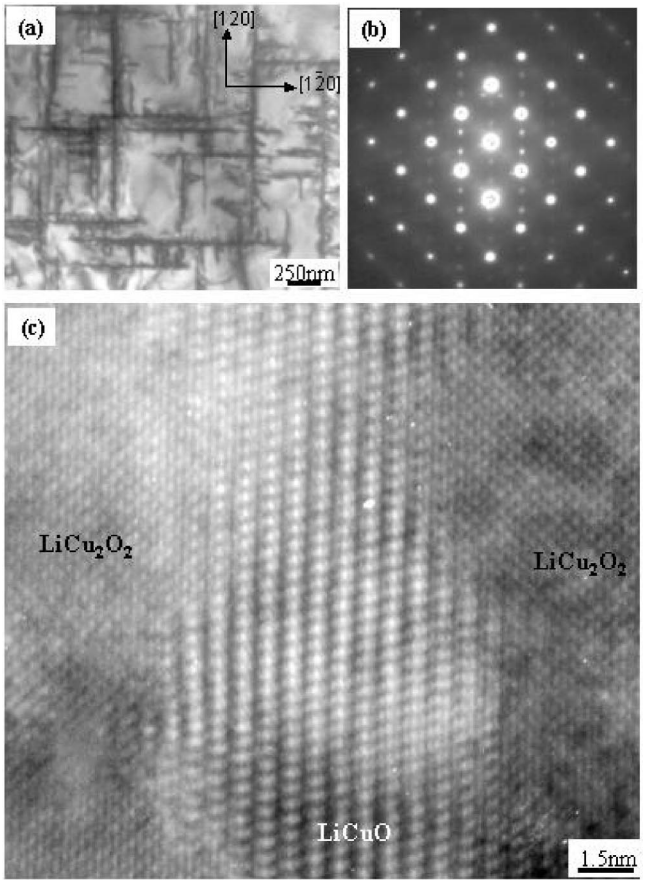

FIG. 2. (a) Bright-field TEM image showing the second-phase precipitates. (b) Selected-area diffraction pattern of $[1\bar{2}2]_{LiCu_2O_2}/[111]_{LiCuO}$. (c) High-resolution TEM image of the precipitate.

state and thus is nonmagnetic. This estimation indicates that the LiCuO phase is less than 10% of the total volume percentage. Figures 2(b) and 2(c) show a selected-area diffraction pattern of $[1\bar{2}2]_{LiCu_2O_2}/[111]_{LiCuO}$ and high-resolution TEM image of the precipitate, respectively. Our observations are consistent with results of earlier analysis of $LiCu_2O_2$, which established the twin-domain structure of this material.[10] No traces of the Li_2CuO_2-impurity phase were found.

Magnetic susceptibility $\chi(T)$ of $LiCu_2O_2$ along different crystallographic directions (measured at the field 1 kOe) is shown in Fig. 3. The temperature dependence of the magnetic susceptibility with a rounded maximum at about 35 K reveals a typical behavior for low-dimensional antiferromagnets. The paramagnetic Curie-Weiss temperature Θ and the Curie constant *C* were extracted from the fit

$$\chi(T)=\chi_{dia}+C/(T+\Theta), \tag{2}$$

$100\ \mathrm{K}<T<300\ \mathrm{K}$. We find $\Theta=81$ K and $C=0.373$ emu K for the magnetic field applied along the *c* direction. For the magnetic field applied in the *ab* plane we find $\Theta=93$ K and $C=0.334$ emu K. The anisotropic behavior of the magnetization may arise from the anisotropy of the exchange inter-

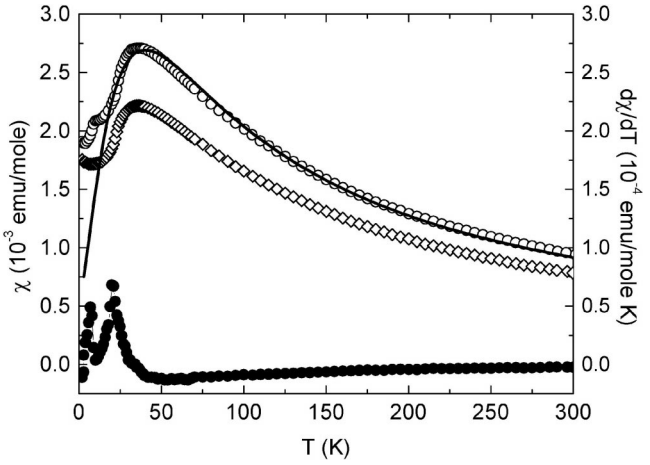

FIG. 3. The temperature dependence of the magnetic susceptibility χ. The open diamonds and circles denote data when magnetic field is applied in the ab plane and parallel to the c axis, respectively. The line is a fit using alternating chain model with the parameters $J_1=43.9$ K and $\delta=0.89$ (see details in the text). The solid circles denote the temperature dependence of $d\chi/dT$; the magnetic field is applied parallel to the c axis.

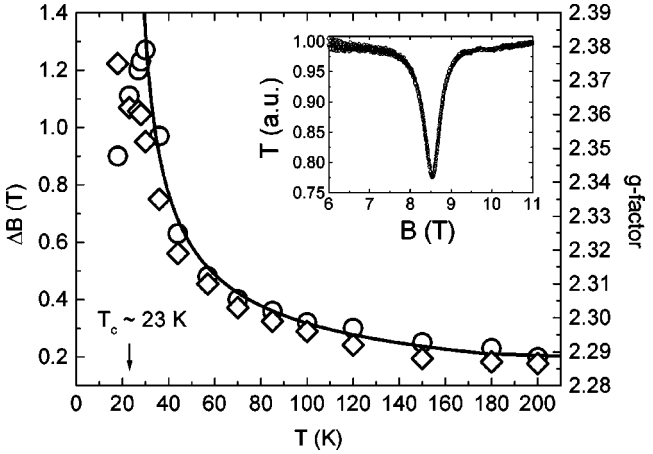

FIG. 4. The ESR linewidth vs temperature at a frequency of 277 GHz (circles). The line is the fit, using Eq. (4). The temperature dependence of the g factor (diamonds). The inset shows typical resonance spectrum at the frequency of 277 GHz and the temperature of 56 K. The line is the Lorentzian fit.

actions in $LiCu_2O_2$. A transition to a long-range-ordered phase is clearly seen in the $d\chi/dT$ vs T dependence, occurring at $T\sim 23$ K. We also found a second low-temperature transition ($T\sim 9$ K), whose origin will be discussed below.

It has been shown[6] that for the dimerized frustrated $S=1/2$ chain, it is impossible to determine all three coupling parameters (J_1, J_2, and δ) from the magnetic susceptibility alone if sufficient low-temperature data are not available. The precise value of the g factor (known from independent experiments, e.g., ESR) is very important. Since the g factor in $LiCu_2O_2$ significantly depends on temperature (addressed below) and the low-temperature behavior of $LiCu_2O_2$ deviates appreciably from that of a purely one-dimensional system, it is difficult to come to a simple conclusion about exchange parameters in this system. In order to analyze the magnetic susceptibility and to get an estimation of the exchange parameters, the simplest alternating-chain model[12] was chosen. The best fit is obtained for the exchange integral $J=43.9$ K and the dimerization parameter $\delta=0.89$ (Fig. 3).

The ESR experiments were performed on a transmission-type millimeter-wavelength band ESR spectrometer with oversized waveguides in a frequency range of 90–370 GHz and in fields up to 14 T. Taking into account the observed peculiarities of the $LiCu_2O_2$ microstructure (i.e., twinning in the ab plane) we chose to apply the magnetic field along the c axis. A sample of a typical size $1\times1\times0.5$ mm^3 was in the Faraday geometry ($h_w\perp B$, where h_w is a magnetic component of the microwave radiation). A distinct resonance absorption with a linear frequency-field dependence was observed at $T>23$ K. A typical absorption spectrum measured at 277 GHz and 56 K is shown in the inset of Fig. 4. The integrated intensity of the resonance has been calculated using a Lorentzian fit and is depicted as a function of the temperature in Fig. 5. One can see a pronounced maximum at $T\sim 45$ K which is a clear signature of transitions within the excited states. Due to spin dimerization, an energy gap Δ opens, separating the spin-singlet ground state from the first excited triplet (inset of Fig. 5). In $S=1/2$ quasi-one-dimensional spin systems the ESR spectrum results basically from transitions between the excited states (in the general case transitions within the entire Brillouin zone should be considered), which are separated from the ground state by the energy gap Δ. The Boltzman distribution is included to analyze the temperature dependence of the ESR signal and determine the singlet-triplet energy gap. For the integrated absorption we can write

$$I(T)\sim\{\exp[(-\Delta+g\mu_B B)/k_B T] - \exp[(-\Delta-g\mu_B B)/k_B T]\}/Z, \quad (3)$$

where g is the g factor, μ_B is the Bohr magneton, k_B is the Boltzmann constant, and Z is the partition function for the

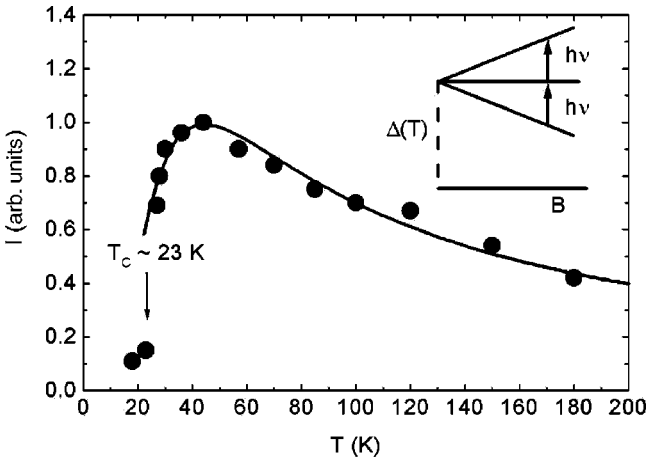

FIG. 5. The integrated resonance intensity vs temperature at a frequency of 277 GHz (a resonance field is about 8.5 T). The solid line is a fit using Eq. (3) with the energy gap $\Delta=72$ K. In the inset we show the singlet-triplet model.

singlet-triplet energy scheme. The best fit of the experimental data gives a mean energy gap Δ between the ground state and the first excited state of 72 K (Fig. 5). As we mentioned above, a gapped dimer liquid phase in the $S=1/2$ spin chain with alternating exchange interactions corresponds to the intermediate range of the J_2/J_1 ratio: $\alpha_{c1}<J_2/J_1<\alpha_{c2}$.

As shown in Fig. 5 the resonance intensity suddenly drops below $T\sim 23$ K. We associate this drop with a collapse of the spin-singlet ground state, which is accompanied by the collapse of the singlet-triplet energy scheme at the lower temperature. This temperature corresponds to the transition to the long-range-ordered magnetic state, observed in both susceptibility and specific-heat experiments.[9–11] Excitations associated with an antiferromagnetic resonance in $LiCu_2O_2$ have been observed in the low-temperature magnetic phase in the frequency range of 20–50 GHz by Vorotinov *et al.*[9] The frequency-field dependence of this absorption deviates from that for an orthorhombic antiferromagnet, suggesting a noncollinear magnetic structure of $LiCu_2O_2$ at low temperatures. This structure might indicate an appearance of ''chiral'' degrees of freedom, due to the frustration of the exchange interaction in the triangular-bond configuration.

A significant broadening (about 6 times) of the resonance line has been observed in $LiCu_2O_2$ with a decrease in the temperature from 180 K to 23 K (Fig. 4). This broadening can be associated with an enhancement of short-range-ordered AFM correlations, followed by a transition into the long-range-ordered state. An increase in the ESR linewidth ΔB with a decreasing temperature can be well described by applying the commonly used formula

$$\Delta B\sim[(T-T_c)/T_c]^{-n}, \tag{4}$$

where T_c is the critical temperature and n is the empiric coefficient. In contrast with results of the X-band (9.4 GHz, $B\sim 0.3$ T) ESR studies (where $n=1.28$),[9] the best fit of the high-frequency ESR (277 GHz, $B\sim 9.5$ T) data is achieved for $n=0.58$. The quantitative dissimilarity in the temperature behavior of the linewidth can be naively understood by taking into account the influence of the high magnetic field. In an exchange-coupled low-D spin system, the magnetic field tends to induce a magnetic order, suppressing quantum fluctuations and thus significantly changing the spin dynamics and relaxation behavior. The larger the field, the larger these changes are. The influence of the external magnetic field on the relaxation processes in low-D spin systems might be of special interest for further theoretical and experimental investigations.

ESR also reveals a pronounced change of the g factor with temperature (Fig. 4). We associate this behavior with two possible factors. First, an enhancement of short-range-ordered correlations can noticeably change a local field on the Cu^{2+}-ion sites, which eventually could cause a change of the g factor. Second, the change of the g factor could be attributed to the significant (~ 2 times) change in the orthorhombic strain $(a-2b)/(a+2b)$, observed in $LiCu_2O_2$ using high-resolution x-ray diffraction measurements ranging from 10 K to 300 K.[11] We suggest that the intensive interplay between the lattice and spin degrees of freedom may play an important role in the spin dynamics and magnetic properties of $LiCu_2O_2$.

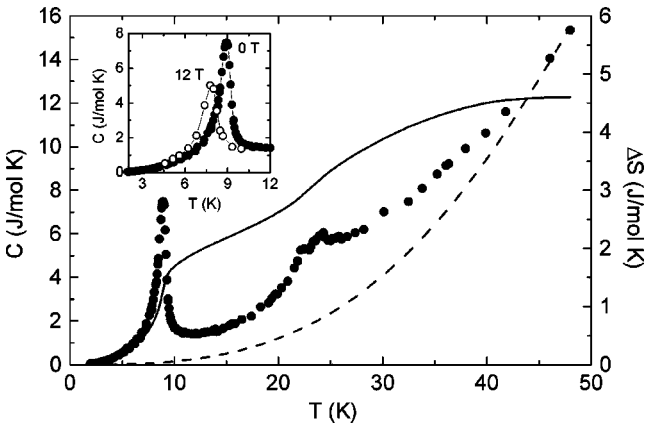

FIG. 6. The temperature dependence of the specific heat (close circles); the dashed line indicates the phonon contribution for $\Theta_D=400$ K. The solid line indicates the entropy removed after subtracting the phonon contribution. The inset shows the low-temperature peak for $B=0$ (solid circles) and 12 T (open circles), where 12 T shifts the peak from 9 K to 7.8 K.

It is known that because of the interchain interaction a transition into the long-range-ordered state can occur in low-D materials at low enough temperatures. In doped low-D materials, such as $CuGe_{1-x}Si_xO_3$,[13] cutting the chains creates additional interchain bonds, enhancing 3D correlations and finally inducing long-range 3D order at low temperature. The transition temperature significantly depends on the doping concentration. Chemical disorder along the spin chains (observed by anisotropic line broadening of the x-ray diffraction peaks[11]) was suggested to play an important role in the magnetic ordering of $LiCu_2O_2$ at $T\sim 23$ K. In accordance with this scenario the Néel temperature should depend significantly on the concentration of chain defects that create disorder. Several crystals were tested, all of which demonstrated similar temperature behavior accompanied by the phase transition at $T\sim 23$ K (which is consistent with T_N obtained by other authors[9,11]). From this observation we conclude that chemical disorder along the spin chains may play an important role in the magnetic properties of $LiCu_2O_2$, but it is quite unlikely to be the main driving force of the $T\sim 23$ K transition.

As mentioned above, the transition at $T\sim 23$ K can be associated with a transition into a long-range-ordered phase with noncollinear magnetic structure. A second transition was observed at 9 K as illustrated by a sharp drop in the magnetic susceptibility when $B\|c$ (see Fig. 3) and a large asymmetric peak in the specific heat. Figure 6 shows this feature along with a smaller and broader doubly peaked anomaly where the peaks appear at 22.5 K and 24.2 K, in excellent agreement with the previous report.[11] The origin of the double-peak structure is not clear at the moment. A Debye function with $\Theta_D=400$ K was used to estimate and then subtract the phonon contribution, and the remaining heat capacity was integrated (as C/T) to determine the entropy ΔS removed at each of the transitions. While at present the au-

thors are not aware of an isostructural, nonmagnetic system for comparison, a $\Theta_D \sim 400$ K is compatible with many of the other cuprates and has minimal impact on the low-temperature results. The entropy removed under the 9 K peak was 1.8 ± 0.1 J/mol K, where changes of Θ_D by ± 30 K shift the entropy by about 1% and the uncertainty arises primarily from varying the treatment of the overlapping tails of the 9 K and 23 K peaks. The large quantity of entropy removed under this peak indicates that this is a property of the bulk material and, thus, an intrinsic effect. This peak is only weakly dependent on magnetic fields, where an applied field of 12 T shifts the peak down in temperature only 1.2 K without apparent broadening, as shown in the inset of Fig. 6. The entropy removed under the peak remains constant at 0 and 12 T within the accuracy of the measurement. The sharpness of the peak, relative insensitivity to large magnetic fields, and conservation of entropy underneath the peak strongly suggest this may be a first-order transition. We hypothesize that the transition might be attributed to further evolution of the magnetic structure in $LiCu_2O_2$, namely, the development of a collinear AFM structure. This scenario seems quite reasonable, if one takes into the account the temperature change of the crystallographic parameters, seen in the change of the orthorhombic strain,[11] and thus the change in the exchange constants. It would be extremely interesting to identify in detail the role of the lattice degrees of freedom in the evolution of the magnetic structure in $LiCu_2O_2$. The shift to lower temperatures in an applied magnetic field is consistent with antiferromagnetism, and the temperature shift of the 9 K peak by ~ 1.2 K in 12 T is reasonable in a system with exchange parameters of order of several tens K. The entropy removed under the peaks near 23 K is more difficult to treat, in part due to the broad nature of the peaks and in part due to the greater sensitivity of the result of changes in Θ_D as well as the tendency of real materials to deviate from a Debye curve [i.e., $\Delta_D(T) < \Delta_D(T=0\ \mathrm{K})$]. However, in the simple picture with $\Delta_D(T) = 400$ K, the broad peaks near 23 K encompass a $\Delta S = 2.8 \pm 0.4$ J/mol K by 40 K, where the larger uncertainty reflects the difficulty of treating the phonon contribution in this temperature region. A suitable nonmagnetic analog will be necessary to enable separation of the phonon contribution and thus permit a detailed study of the thermodynamic properties corresponding to the 23 K transition.

In conclusion, we have reported on the investigation of the structure, resonance, magnetic, and thermodynamic properties of the quasi-low-D quantum AFM compound $LiCu_2O_2$, which may be regarded as a good candidate for a quantum $S = 1/2$ chain with competing nearest- and next-nearest-neighbor interactions in the intermediate range of the J_2/J_1 ratio ($\alpha_{c1} < J_2/J_1 < \alpha_{c2}$). The ESR results show that at $T > 23$ K $LiCu_2O_2$ has a spin-singlet ground state with a finite energy gap of $\Delta \sim 72$ K that separates the first excited triplet from the singlet ground state. The spin-singlet ground-state collapse has been revealed at a temperature below ~ 23 K. In addition, a second low-temperature transition was observed at $T \sim 9$ K, indicative of further development of the magnetic structure. A neutron scattering study will be very helpful in determining the exact magnetic structure and the coupling parameters in $LiCu_2O_2$ across the different regions of its phase diagram.

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