Magnetic Phase Transitions in the double spin-chains compound $\text{LiCu}_2\text{O}_2$

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Abstract

We report high-resolution x-ray diffraction, muon-spin-rotation spectroscopic and specific heat measurements in the double spin-chains compound $\text{LiCu}_2\text{O}_2$. The x-ray diffraction results show that the crystal structure of $\text{LiCu}_2\text{O}_2$ is orthorhombic down to $T=10\text{K}$. Anisotropic
line-broadening of the diffraction peaks is observed, indicating disorder along the spin chains. Muon spin relaxation and specific heat measurements show that LiCu$_2$O$_2$ undergoes a phase transition to a magnetic ordered state at $T_1 \sim 24$K. The specific heat data exhibits a second $\lambda$-like peak at $T_2 \sim 22.5$K, which increases with increasing magnetic field similarly way to that found in spin-ladder compounds.

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1 Introduction

One-dimensional $S=\frac{1}{2}$ antiferromagnets have physical properties which can only be accounted for by quantum effects. The ground-state and the spectrum of excitations of a Heisenberg spin-chain with nearest-neighbors interaction are known exactly and the theoretical results are in good agreement with experiments [1]. Compounds with coupled $S=1/2$ chains are the subject of intense investigations as they represent intermediate structures between one- and two-dimensional compounds. In this class of materials, antiferromagnetic long-range order has been observed for compounds with zig-zag chains like SrCuO$_2$ [3] or with weak inter-chains exchange interactions like Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$ [2]. A common property of these materials is that both the size of the magnetic moments at saturation and the Néel temperature are strongly reduced due to frustration between exchange integrals and quantum fluctuations [2]. In addition, understanding the magnetic properties of coupled-chains compounds is of interest for copper-oxides high-$T_c$ superconductors, which can be considered as two-dimensional spin-$\frac{1}{2}$ antiferromagnets with carrier doping.

LiCu$_2$O$_2$ is a mixed-valent compound with copper ions in the Cu$^{2+}$ and Cu$^{1+}$ oxidation states [5]. At first the chemical structure of LiCu$_2$O$_2$ was described within the tetragonal space group $P4_2/nmc$ [6]. Later x-ray and neutron measurements [7] suggested that LiCu$_2$O$_2$ crystallizes in the orthorhombic space-group $Pnma$ with lattice constants $a=5.72$ Å, $b=2.86$ Å and $c=12.4$ Å at room temperature. The chemical structure of LiCu$_2$O$_2$ may be viewed as chains of Cu$^{2+}$ ions propagating along the b-axis. There are two such parallel Cu-chains which run along the a-axis and which are bridged along the c-axis by a 90° oxygen bond, as shown in Fig.1. The double-chains are well isolated from each other by both Li-ions and sheets of non-magnetic Cu$^{1+}$ ions. From these considerations, it appears that LiCu$_2$O$_2$ is a good candidate for either a spin-ladder or a zig-zag chain system, depending on the ratio of the nearest- to second-nearest neighbor exchange interactions. In this paper, we report high-resolution x-ray powder diffraction, muon-spin-rotation spectroscopy ($\mu$SR) and specific heat results in the spin-$\frac{1}{2}$ chain-like compound LiCu$_2$O$_2$. The results suggest that antiferromagnetic ordering is induced by chemical disorder along the chains.
2 Experimental results and Discussion

Single-crystals were prepared by the spontaneous crystallization method starting from Li$_2$CO$_3$ and CuO. A detailed description of the preparation method is given elsewhere [8]. For the experiments reported here, single-crystals of typical size 3 $\times$ 3 $\times$ 1 mm$^3$ were used. Special care is to be taken because LiCu$_2$O$_2$ oxidizes in open air. Therefore, the samples were kept under dry helium atmosphere. X-ray diffraction with Cu K$_\alpha$ radiation showed that the single crystals contain traces of Li$_2$CuO$_2$ ($\sim$3%). The structural and magnetic properties of Li$_2$CuO$_2$ are well established [9] and can easily be separated from those of LiCu$_2$O$_2$.

The high-resolution x-ray diffraction experiments were performed at the Swiss-Norwegian Beam line at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A diffraction Debye-pattern was collected in standard Scherrer geometry with a wave length of $\lambda$=0.49876 Å at room temperature. The 2$\theta$ resolution was improved to 0.01$^\circ$ by means of four Si (111) analyzer crystals. For the low temperature experiments a $^4$He-flow cryostat was installed to cool the sample down to 10 K. The experiments at low temperatures were performed with $\lambda$=0.79764 Å. Fine powder of LiCu$_2$O$_2$ was sealed in a 0.3 mm diameter quartz capillary. The $\mu$SR experiments were performed on the GPS spectrometer at the Paul-Scherrer Institut, Switzerland. The sample consisted of approximately 10 crystals which were glued on a silver plate with the crystallographic c-axis oriented along the muon path. A $^4$He flow-cryostat was used to obtain temperatures between 10K $\leq T \leq$ 30K. The calorimetric measurements were performed with a commercial PPMS (Quantum Design) device in the temperature range 1.8K $\leq T \leq$100K. Fig. 2 shows the splitting of the 400 and 200 reflections determined at T= 10K. This splitting is a direct evidence that the chemical structure of LiCu$_2$O$_2$ is orthorhombic. Diffraction reflections with Miller indices $h, k \neq 0$ are found to be broader than those with $h=0, k=0$. This anisotropic line-broadening indicates atomic disorder in the crystallographic (a,b)-plane. The in-plane correlation length, as calculated from the half-width at half maximum of the Bragg peaks, amounts to $\sim$540Å. The orthorhombic strain $(a^*-b^*)/(a^*+b^*)$ distinctly decreases from room temperature to T=10K by a factor of $\sim 2$, which is not expected (see Fig. 3). Usually, materials exhibit the tendency to approach higher symmetries for increasing temperatures as the increase of the
lattice vibrations as a function of temperature leads to the relaxation of the lattice and to the reduction of the strain. From an extended diffraction pattern taken at room temperature, we conclude that the chemical structure of LiCu$_2$O$_2$ is well described with the space group $Pnma$ and lattice constants $a=5.7301(2)$ Å, $b=2.8594(1)$ Å and $c=12.4192(3)$ Å. The understanding of the temperature dependence of the strain, however, requires a more detailed structural studies at elevated temperatures.

In μSR experiments the asymmetric emission of positrons arising from the weak decay of implanted spin-polarized muons is monitored. The time-dependent positron rate $N(t)$ is recorded as a function of time and is given by the function

$$N(t) = N(0) \exp\left(-t/\tau\right)[1 + AG_z(t)],$$

where $A$ is the initial muon asymmetry parameter, $G_z(t)$ the asymmetry function and $\tau$ is the muon lifetime. Zero-field μSR signals in LiCu$_2$O$_2$ are shown in Fig.4. At $T=28$ K, the asymmetry function does not reveal frequencies, indicating that the magnetic moment of the implemented muon does not undergo Larmor precession. In this temperature regime, the muon spin depolarization originates from the magnetic fields caused by the Cu nuclear dipole moments. Assuming that these internal fields have a Gaussian distribution and that they are randomly oriented, the asymmetry function $G_z(t)$ is given by the familiar Kubo-Toyabe expression

$$G_{KT}(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2) \exp\left(-\frac{1}{2} \Delta^2 t^2\right),$$

where $\Delta^2/\gamma^2_\mu$ represents the second moment of the field distribution and $\gamma_\mu = 2\pi \cdot 13.553879$ kHz/G is the giromagnetic ratio of the muon. At $T=28$ K, a fit to the μSR data yields a dipolar width $\Delta = 0.324$ (MHz).

Upon lowering the temperature below $T_1 \sim 24$K, a precession of the muon spins is observed. This suggests that the Cu$^{2+}$ spins develop a static magnetic order below that temperature. A characteristic feature of the muon signal determined in LiCu$_2$O$_2$ at low temperatures is that the frequencies show a damping as a function of increasing decay time, which indicates a broad distribution of magnetic fields at the muon stopping sites. In the temperature range $10$K $\leq T \leq 24$K, the data are best described by assuming for $G_z(t)$ the form

$$G_z(t) = A_1 \exp[-(\lambda t)]$$
\[ f(t) = A e^{-\gamma_1 t} \cos(2\pi \omega_1 t + \phi) + A e^{-\gamma_2 t} \cos(2\pi \omega_2 t + \phi). \] (3)

\( \phi \) is given by the position of the positron detectors relative to the muon polarization. The first term of Eq. 3, which arises from the non-zero projection of the muon-spin polarization along the direction of the internal fields, indicates the presence of fast longitudinal fluctuations in \( \text{LiCu}_2\text{O}_2 \). This suggests that even in the ordered magnetic phase the \( \text{Cu}^{2+} \) magnetic moments are not fully static. A least-square fit to the muon data in the temperature range \( 10K \leq T \leq 23K \) with Eq. 3 yields essentially temperature independent parameters apart from the Larmor frequencies. They show a dependence as a function of temperature reminiscent of static order parameters measured in ordered ferro- or antiferromagnets (Fig. 5). The fitted values for the relaxation rates are \( \lambda = 0.14 \text{ MHz}, \gamma_1 \sim 5.5 \text{ MHz} \) and \( \gamma_2 \sim 7 \text{ MHz} \), respectively. In the temperature range \( 22K \leq T \leq 24K \), the relaxation rate \( \lambda \) increases which indicates that the magnetic moments in \( \text{LiCu}_2\text{O}_2 \) fluctuate faster when approaching the ordering temperature \( T_1 = 24K \). The fact that the damping of the muon spin precession is temperature independent below \( T \leq 19K \) indicates that some static inhomogeneity in the \( \text{Cu}^{2+} \) magnetic moments along the spin-chains is present in \( \text{LiCu}_2\text{O}_2 \). A similar situation is encountered in Zn- and Si-doped \( \text{CuGeO}_3 \), where it has been shown that impurities along the spin-chains result in spatial variation of the size of the magnetic moments around the doping center [11]. Accordingly, staggered moments will be induced along the spin-chains which eventually leads to static Néel order [12]. This point of view has been adopted in a previous study of the magnetic properties of \( \text{LiCu}_2\text{O}_2 \) by magnetic susceptibility and resonance measurements [8]. The magnetic susceptibility of \( \text{LiCu}_2\text{O}_2 \) shows a broad maximum around \( T \sim 50K \). As the temperature dependence of the magnetic susceptibility is well reproduced with a Heisenberg model for interacting chains [8, 13], it has been concluded that \( \text{LiCu}_2\text{O}_2 \) is a low-dimensional system of spin-ladder type. A \( S = \frac{1}{2} \) spin-ladder structure has a singlet ground-state [14] and as such does not develop long-range order. However, antiferromagnetic resonance lines were observed in \( \text{LiCu}_2\text{O}_2 \) by the authors of Ref. [8] below \( T=22.5K \). It was therefore argued that \( \text{LiCu}_2\text{O}_2 \) is an antiferromagnet below \( T_N \sim 22.5K \) as a consequence of partial redistribution of copper and lithium ions along the chains. On the other hand, antiferromagnetic ordering in \( \text{LiCu}_2\text{O}_2 \) might also be due to small interchain interactions.
In that context, mean-field theory \[15\] applied to the special of coupled-chains predicts a Néel temperature \(T_N\) proportional to \(J_{\text{perp}}\). In the absence of precise exchange interactions between the \(\text{Cu}^{2+}\) for \(\text{LiCu}_2\text{O}_2\), it is however difficult to draw definite conclusions at this stage about the origin of antiferromagnetic ordering in \(\text{LiCu}_2\text{O}_2\). Inelastic neutron measurements are therefore desirable. The \(\mu\text{SR}\) results clearly indicate that \(\text{LiCu}_2\text{O}_2\) undergoes a phase transition to an ordered magnetic state below \(T_1=24\text{K}\). A close look at the temperature dependence of the Larmor frequencies shown in Fig.\[5\] also reveals another anomaly around \(T_2=22.5\text{K}\). The specific heat results are shown in Fig.\[8\]. A double peak structure is observed in the temperature dependence of the specific heat with maxima at \(T_2=22.5\text{K}\) and \(T_1=24\text{K}\). The specific heat of \(\text{LiCu}_2\text{O}_2\) exhibits sharp \(\lambda\)-like peaks which have different dependencies as a function of applied magnetic field. The peak at \(T_1=24\text{K}\) shifts to lower temperatures when a field is applied and is therefore associated to the magnetic phase transition. On the other hand the \(T_2=22.5\text{K}\) peak does not exhibit any temperature shift but significantly increases as a function of magnetic field.

In conclusion, we have presented high-resolution x-ray powder diffraction, \(\mu\text{SR}\) and specific heat measurements in \(\text{LiCu}_2\text{O}_2\). The data are consistent with the view that \(\text{LiCu}_2\text{O}_2\) can be considered as a double-chains \(S = \frac{1}{2}\) system for which Néel ordering below \(T_N = 24\text{K}\) is induced by chemical disorder along the spin-chains. The field dependence of the specific heat data shows features similar to the ones observed in spin-ladder compounds.

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Figure 1: Chemical structure of LiCu$_2$O$_2$ showing the double Cu$^{2+}$ chains.

Figure 2: (left) Selected reflections of the x-ray pattern taken at T=20K in LiCu$_2$O$_2$ which shows the anomalous broadening of the (210) Bragg reflection. The 006 peak was shifted by $\sim$0.5° to obtain a superposition of these reflections. (right) 400 and 020 reflections reflecting the orthorhombic distortion. The lines are fits with a Voigt function.

Figure 3: Orthorhombic strain determined in LiCu$_2$O$_2$. See text for details.

Figure 4: Experimental zero-field $\mu$SR signal measured in LiCu$_2$O$_2$ on GPS. The line is the result of a fit with the model function explained in the text.

Figure 5: Larmor frequencies observed in LiCu$_2$O$_2$ on GPS. The lines are guides to the eyes.

Figure 6: Specific heat data measured in LiCu$_2$O$_2$. The inset depicts the dependence of the $\lambda$-like peak for increasing and decreasing magnetic fields at $T_2=22.5$K.
Strain \( \frac{(a^*-b^*)}{(a^*+b^*)} \) vs. T (K)
