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Magnetic phase transitions in the double spin-chains compound $LiCu_2O_2$

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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 $LiCu_2O_2$. The X-ray diffraction results show that the crystal structure of $LiCu_2O_2$ is orthorhombic down to $T = 10$ 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 $LiCu_2O_2$ undergoes a phase transition to a magnetic ordered state at $T_1 \sim 24$ K. The specific heat data exhibits a second λ-like peak at $T_2 \sim 22.5$ K, which increases with increasing magnetic field in a similar 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 $S = \frac{1}{2}$ 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_2CuO_3 and Ca_2CuO_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 [4,5]. In addition, understanding the magnetic properties of coupled-chains compounds is of interest for

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copper-oxides high-T_c superconductors, which can be considered as two-dimensional spin-$\frac{1}{2}$ antiferromagnets with carrier doping.

$LiCu_2O_2$ is a mixed-valent compound with copper ions in the Cu^{2+} and Cu^{1+} oxidation states [6]. At first the chemical structure of $LiCu_2O_2$ was described within the tetragonal space group $P4_2/nmc$ [7]. Later X-ray and neutron measurements [8] suggested that $LiCu_2O_2$ 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 $LiCu_2O_2$ 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 $LiCu_2O_2$ 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 (μSR) and specific heat results in the spin-$\frac{1}{2}$ chain-like compound $LiCu_2O_2$. The results suggest that antiferromagnetic ordering is induced by chemical disorder along the chains.

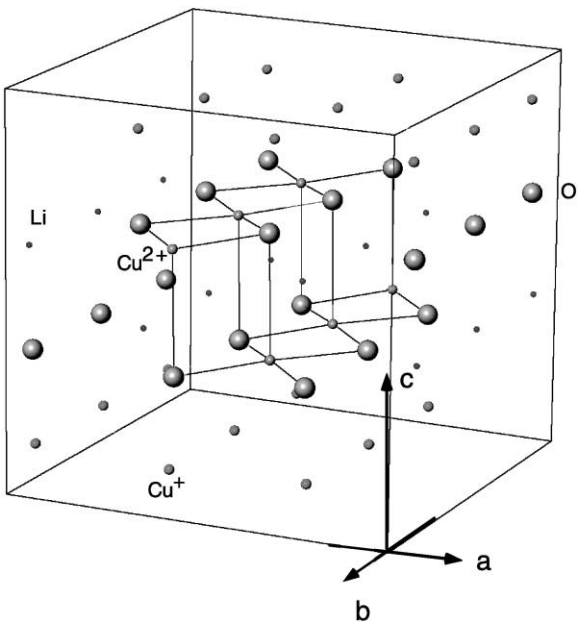

Fig. 1. Chemical structure of $LiCu_2O_2$ showing the double Cu^{2+} chains.

2. Experimental results and discussion

Single crystals were prepared by the spontaneous crystallization method starting from Li_2CO_3 and CuO. A detailed description of the preparation method is given elsewhere [9]. 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 $LiCu_2O_2$ oxidizes in open air. Therefore, the samples were kept under dry helium atmosphere. X-ray diffraction with Cu K_α radiation showed that the single crystals contain traces of Li_2CuO_2 (~3%). The structural and magnetic properties of Li_2CuO_2 are well established [10,11][1] and can easily be separated from those of $LiCu_2O_2$.

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 2θ resolution was improved to 0.01° by means of four Si (1 1 1) 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 $LiCu_2O_2$ was sealed in a 0.3 mm diameter quartz capillary. The μSR 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 $10\ \text{K} \leqslant T \leqslant 30$ K. The calorimetric measurements were performed with a commercial PPMS (Quantum Design) device in the temperature range $1.8\ \text{K} \leqslant T \leqslant 100$ K. Fig. 2 shows the splitting of the 400 and 020 reflections determined at $T = 10$ K. This splitting is a direct evidence that the chemical structure of

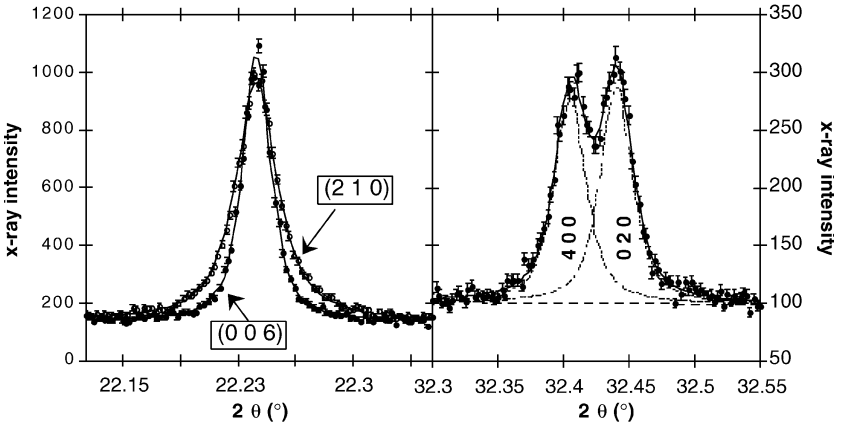

Fig. 2. (left) Selected reflections of the X-ray pattern taken at $T = 20$ K in $LiCu_2O_2$ which shows the anomalous broadening of the (2 1 0) Bragg reflection. The 006 peak was shifted by $\sim 0.5^\circ$ to obtain a superposition of these reflections. (right) 400 and 020 reflections reflecting the orthorhombic distortion. The lines are fits with a Voigt function.

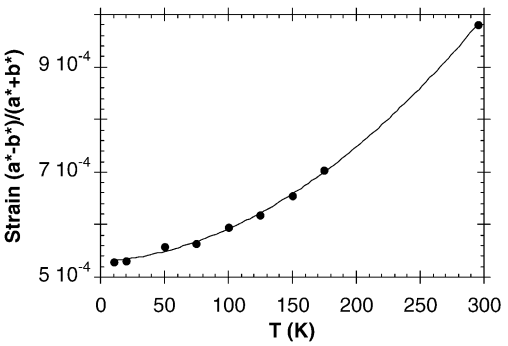

Fig. 3. Orthorhombic strain determined in $LiCu_2O_2$. $a^* = a$ and $b^* = 2b$ with a and b the lattice constants. See text for details.

$LiCu_2O_2$ 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 ~ 540 Å. The orthorhombic strain $(a^* - b^*)/(a^* + b^*)$ distinctly decreases from room temperature to $T = 10$ K by a factor of ~ 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 $LiCu_2O_2$ 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

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

where A is the initial muon asymmetry parameter, $G_z(t)$ the asymmetry function, τ the muon life-time and B is a time-independent background. Zero-field μSR signals in $LiCu_2O_2$ 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 depolarisation originates from the magnetic fields caused by the Cu nuclear dipole moments. Assuming that at the muon site these internal fields have a Gaussian distribution and that they are randomly oriented, the asymmetry

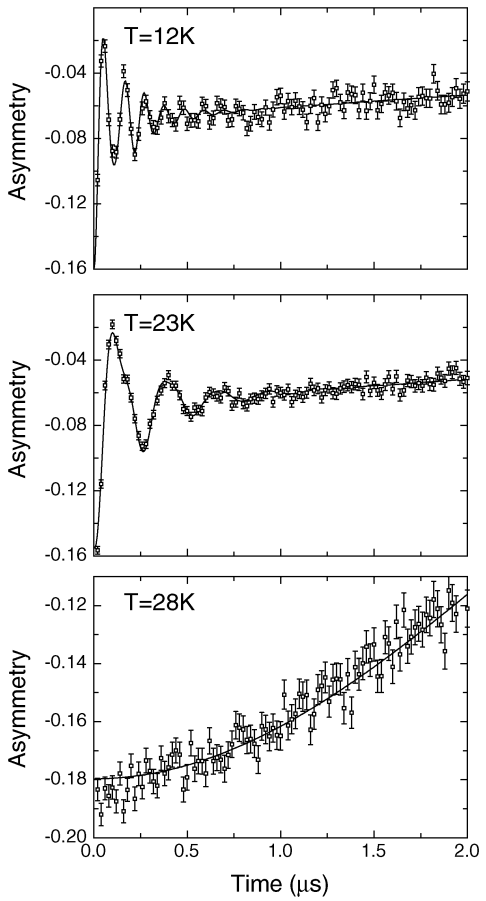

Fig. 4. Experimental zero-field μSR signal measured in $LiCu_2O_2$ on GPS. The line is the result of a fit with the model function explained in the text.

function $G_z(t)$ is given by the familiar Kubo–Toyabe expression [12]

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

where Δ^2/γ_μ^2 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 $\Delta = 0.324(3)$ MHz. Upon lowering the temperature below $T_1 \sim 24$ K, a spontaneous 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 $LiCu_2O_2$ 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 $10\ \text{K} \leqslant T \leqslant 24$ K, the data are best described by assuming for $G_z(t)$ the form

$$G_z(t) = A_1 \exp[-(\lambda t)] + A_{f1} e^{-\gamma_1 t}\cos(2\pi\omega_1 t + \phi) + A_{f2} e^{-\gamma_2 t}\cos(2\pi\omega_2 t + \phi), \qquad (3)$$

where the phase ϕ is essentially 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 $LiCu_2O_2$. This suggests that even in the ordered magnetic phase the Cu^{2+} magnetic moments are not fully static. The occurrence of two distinct oscillatory components in the μSR signal points to the presence of magnetically non-equivalent muon stopping sites. A least-squares fit to the muon data in the temperature range $10\ \text{K} \leqslant T \leqslant 22$ K 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 magnets (Fig. 5). The fitted values for the relaxation rates are $\lambda = 0.14$ MHz, $\gamma_1 \sim 5.5$ MHz and $\gamma_2 \sim 7$ MHz, respectively. In the temperature range $22\ \text{K} \leqslant T \leqslant 24$ K, the relaxation rate λ increases which indicates that the magnetic moments in $LiCu_2O_2$ fluctuate faster when approaching the ordering temperature $T_1 = 24$ K. The fact that the damping of the muon-spin precession is temperature independent in the magnetic state indicates that some static inhomogeneity in the Cu^{2+} magnetic moments along the spin-chains is present in $LiCu_2O_2$. A similar situation is encountered in Zn- and Si-doped $CuGeO_3$, 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 [13]. Accordingly, staggered moments will be induced along the spin-chains which eventually leads to static Néel

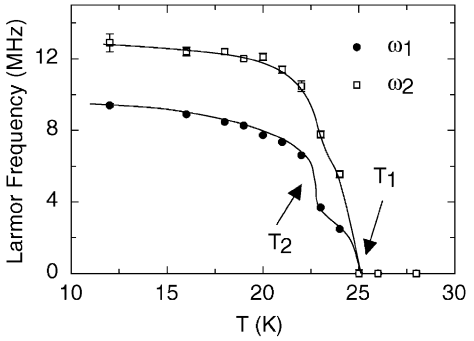

Fig. 5. Larmor frequencies ω_1 and ω_2 for the two different muon-stopping sites observed in $LiCu_2O_2$ on GPS. The lines are guides to the eyes.

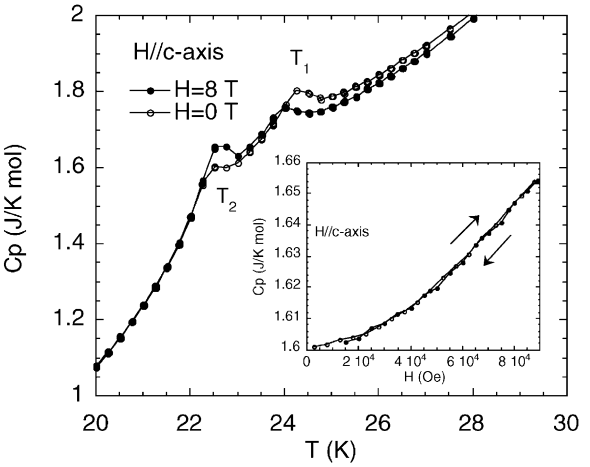

Fig. 6. Specific heat data measured in $LiCu_2O_2$. The inset depicts the dependence of the λ-like peak for increasing and decreasing magnetic fields at $T_2 = 22.5$ K.

order [14]. This point of view has been adopted in a previous study of the magnetic properties of $LiCu_2O_2$ by magnetic susceptibility and resonance measurements [9]. The magnetic susceptibility of $LiCu_2O_2$ shows a broad maximum around $T \sim 50$ K. As the temperature dependence of the magnetic susceptibility is well reproduced with a Heisenberg model for interacting chains [9,15], it has been concluded that $LiCu_2O_2$ is a low-dimensional system of spin-ladder type. A $S = \frac{1}{2}$ spin-ladder structure has a singlet ground-state [16] and as such does not develop long-range order. However, antiferromagnetic resonance lines were observed in $LiCu_2O_2$ by the authors of Ref. [8] below $T = 22.5$ K. It was therefore argued that $LiCu_2O_2$ is an antiferromagnet below $T_N \sim 22.5$ K as a consequence of partial redistribution of copper and lithium ions along the chains. On the other hand, antiferromagnetic ordering in $LiCu_2O_2$ might also be due to small interchain interactions $J_{perp.}$. In that context, mean-field theory [17] applied to the special case of coupled-chains predicts a Néel temperature T_N proportional to $J_{perp.}$. In the absence of precise exchange interactions between the Cu^{2+} for $LiCu_2O_2$, it is however difficult to draw definite conclusions at this stage about the origin of antiferromagnetic ordering in $LiCu_2O_2$. Inelastic neutron measurements are therefore desirable. The μSR results clearly indicate that $LiCu_2O_2$ undergoes a phase transition to an ordered magnetic state below $T_1 = 24$ K. A close look at the temperature dependence of the spontaneous Larmor frequencies shown in Fig. 5 also reveals another anomaly around $T_2 = 22.5$ K. The specific heat results are shown in Fig. 6. A double peak structure is observed in the temperature dependence of the specific heat with maxima at $T_2 = 22.5$ K and $T_1 = 24$ K. The specific heat of $LiCu_2O_2$ exhibits sharp λ-like peaks which have different dependencies as a function of applied magnetic field. The peak at $T_1 = 24$ K shifts to lower temperatures when a field is applied and is therefore associated to the magnetic phase transition. On the other hand the $T_2 = 22.5$ K peak does not exhibit any temperature shift but significantly increases as a function of magnetic field.

3. Conclusion

We have presented high-resolution X-ray powder diffraction, μSR and specific heat measurements in $LiCu_2O_2$. The data are consistent with the view that $LiCu_2O_2$ can be considered as a double-chains $S = \frac{1}{2}$ system for which Néel ordering below $T_N = 24$ 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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