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Antiferromagnetic ordering in Cu_2OCl_2 studied by the muon spin rotation/relaxation technique

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Abstract
We report on muon spin rotation/relaxation (μSR) studies of the cuprate mineral melanothallite, Cu_2OCl_2, over a temperature range between 4.1 and 300 K. This compound has a pyrochlore-like corner-shared OCu_4 tetrahedral network with an $S = 1/2$ system. The magnetic susceptibility shows a broad maximum around 140 K and drops at 70 K. In the μSR measurement, we observed clear muon spin precession spectra below 70 K that is evidence for a long-range magnetic ordered state. However, the time spectra also exhibit exponential damping even in the ordered state, suggesting a possible influence of geometrical frustration in this compound. This renders the need for careful examination of the magnetic structure of the ordered state.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The study of insulating magnetic materials has been at the forefront of condensed-matter physics from the experimental and theoretical points of view, due to their exotic physical properties. Copper oxides, such as quasi-one-dimensional spin chains or spin ladders, have been attracting a great deal of interest because of their unique low-temperature properties. For example, the low-temperature phase of $CuGeO_3$ represented spin–Peierls transition by dimerized $S = 1/2$ chains [1], and Shastry–Suterland lattice with orthogonally arranged spin dimers and a frustrating interdimer coupling realized in $SrCu_2(BO_3)_2$ [2]. Recently, Zheng and co-workers reported a new geometrically frustrated system in a clinoatacamite, $Cu_2Cl(OH)_3$ [3, 4]. Compounds containing Cu^{2+} ions have been extensively studied because

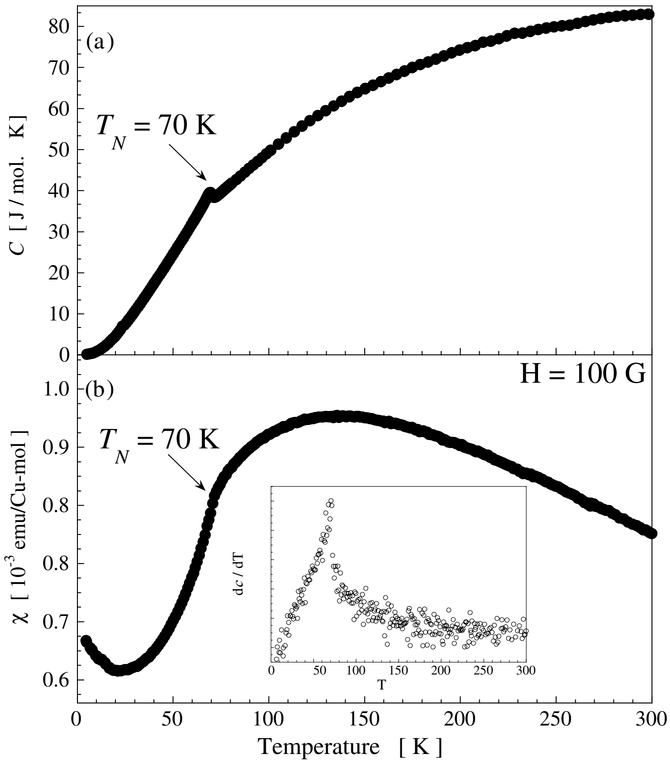

Figure 1. Temperature dependence of (a) heat capacity C and (b) magnetic susceptibility χ in Cu_2OCl_2. The inset shows $d\chi/dT$ as a function of temperature.

they present a large variety of spin phenomena induced by geometrically atomic arrangements. We focused our attention on Cu_2OCl_2 (the cuprate mineral melanothallite), having a similarity to $Cu_2Cl(OH)_3$ in crystal structure.

The crystal structure of Cu_2OCl_2 may be described as OCu_4 oxocentered tetrahedra units linked with each other through the sharing of Cu corners into a pyrochlore-like framework, containing Cl anions [5, 6]. In a previous publication, we reported the physical properties of Cu_2OCl_2 [7]. In order to obtain a unique insight into the magnetic properties, we performed muon spin rotation/relaxation (μSR) measurements on a polycrystalline Cu_2OCl_2. μSR is a powerful technique to detect the local magnetic field and associated spin dynamics in magnetic materials, and it is extremely sensitive to magnetic ordering and local field fluctuations/distributions in quantum magnets.

2. Experimental details

The polycrystalline Cu_2OCl_2 was prepared using CuO (99.999%) and $CuCl_2$ (99.995%), heated at 350 °C in CO_2 atmosphere for 24 h. Powder x-ray diffraction analysis confirmed the single-phased nature of our samples. μSR measurements were performed using spin-polarized muons (μ^+) and a conventional He gas flow mini-cryostat (covering above 4.1 K) at Meson Science Laboratory (KEK-MSL, Japan). The polycrystalline Cu_2OCl_2 powder was wrapped in an Al sheet to avoid deterioration of the specimen by air and moisture. The specimen was mounted on a sample holder and placed in a cryostat. Zero-field (ZF)-μSR spectra were obtained at

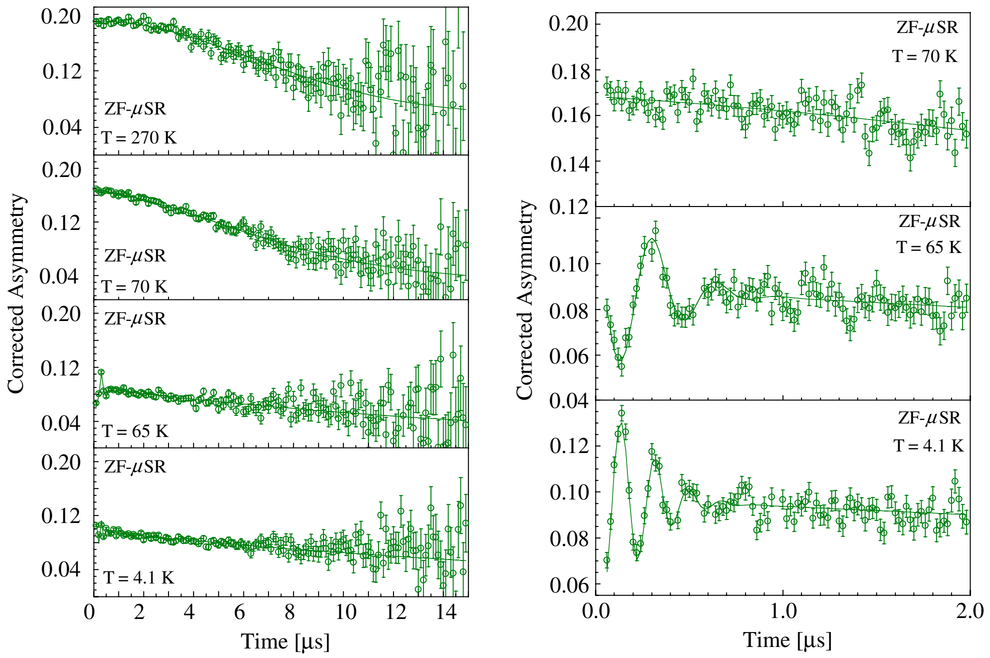

Figure 2. Muon depolarization at typical temperatures. Long-term (left) and short-term (right) time spectra. Solid curves represent those obtained by fitting with equation (1).

temperatures between 4.1 and 300 K. TF-μSR measurements have been performed at 75 K and room temperature for the correction of instrumental asymmetry.

3. Experimental results and discussion

Figure 1 shows the temperature dependence of the heat capacity and magnetic susceptibility in Cu_2OCl_2. The magnetic susceptibility shows a broad maximum around 140 K, and a clear kink is evident at 70 K accompanying a small heat capacity jump.

Figure 2 shows the ZF-μSR time spectra for Cu_2OCl_2 at the respective temperatures. The muon spin polarization is proportional to the corrected asymmetry of the positron decay, $G_z(t) \propto A(t)$. The time spectra over the temperature range between 70 and 270 K have a Gaussian shape due to the nuclear dipole field, and the initial asymmetry is slightly suppressed with decreasing temperature. We confirmed clear muon spin precession signals below 65 K, indicating the appearance of long-range magnetic order. These time spectra were analysed by the following form over the entire temperature range:

$$P(t) = A_1 \exp[-(\sigma t)^2] \cos(ft + \phi) + A_2 \exp(\lambda t) + A_B \qquad (1)$$

where A_i refers to the asymmetry of muons stopped in the sample, σ and λ are the relaxation rates, f is the muon spin precession frequency, ϕ is the initial phase and A_B is the background. The best fit by equation (1) is displayed in figure 2. The muon spin precession frequency f, corrected asymmetry and muon spin relaxation rate σ are displayed as a function of temperature in figure 3. The dashed curve for f in figure 3(a) is the fitting result with a form $f(T) = f(0)(1 - T/T_N)^\beta$, which yields $T_N = 70.1$ K and $f(0) = 6.0$ MHz. The obtained T_N is consistent with the temperature at which the oscillation signals appear. The corrected

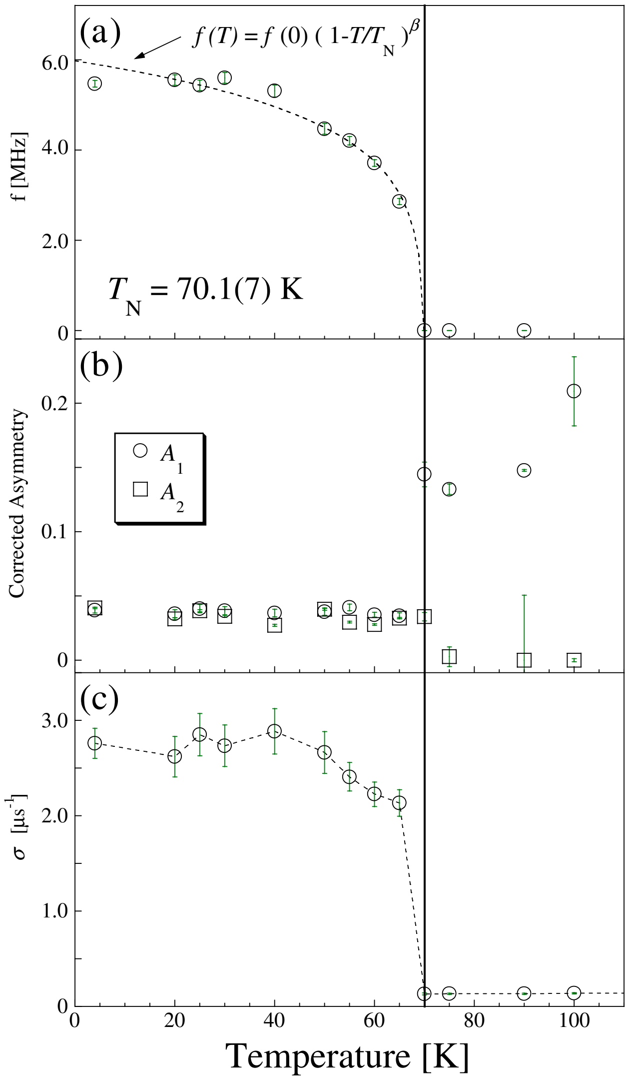

Figure 3. Temperature dependence of (a) muon spin precession frequency f, (b) corrected asymmetry and (c) muon spin relaxation rate σ. The dashed curve is the result of fitting by $f(T) = f(0)(1 - T/T_N)^{\beta}$.

asymmetry A_1 and A_2 change clearly at 70 K, and f and σ exhibit a steep enhancement with decreasing temperature due to the presence of long-range magnetic order. In addition, λ slowly increases above T_N. These results give clear evidence for the onset of antiferromagnetic ordering in Cu_2OCl_2 at 70 K, which is in good agreement with the bulk properties shown in figure 1. The initial asymmetry below 70 K rapidly decreases, which is understood by considering the limited time resolution of 50 ns in using a pulsed muon beam. Thus, the loss of initial asymmetry suggests that the internal magnetic fields are larger than the detection limit of $\sim$500 G (equivalent to maximum precession frequency $\sim$7 MHz) at certain muon sites.

The magnetic ordering in Cu_2OCl_2 is well understood by considering an antiferromagnetic state, because the time spectra below 70 K show clear muon spin precession signals under zero external field. The internal magnetic field at the muon site, B_μ, is estimated to be approximately 450 G from the relationship between f and B_μ, $f = \gamma_\mu B_\mu$, where γ_μ is the gyromagnetic ratio of the muon (=135.54 MHz T^{-1}). However, it is noticeable that these spectra also exhibit an exponential damping (without oscillation), which is described as a 'tail' in equation (1) (see figure 2). This longitudinal spin relaxation might be due to dynamical fluctuation of internal fields. The value of λ below 70 K is about 0.05 MHz, which yields a roughly estimated correlation time of fluctuation, $\tau \sim 1.7 \times 10^{-11}$ s. In this regard, it is interesting to note that Cu_2OCl_2 has a pyrochlore-like lattice which causes geometrical frustration among local magnetic moments. The above behaviour might offer a hint for the possible influence of such a geometrical frustration [8–10].

4. Summary

In summary, we studied the magnetic properties of a melanothallite, Cu_2OCl_2, using μSR technique. The observation of clear muon spin precession signals below 70 K is perfectly in line with the onset of antiferromagnetic order at the transition temperature determined by bulk measurements. From the temperature dependence of f, corrected asymmetry and σ, we confirmed the growth of an antiferromagnetic ordered state below 70 K. In the ordered state, the time spectra below 70 K also exhibit an exponential damping, suggesting a possible influence of geometrical frustration in this compound.

Acknowledgments

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