Coexistence of Long-Range Order and Spin Fluctuation in Geometrically Frustrated Clinoatacamite $Cu_2Cl(OH)_3$

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Muon spin rotation experiments are carried out on clinoatacamite, $Cu_2Cl(OH)_3$, which is a new geometrically frustrated system featuring a three-dimensional network of corner-sharing tetrahedral $3d$ Cu^{2+} spins. A long-range antiferromagnetic order occurs below 18.1 K with a surprisingly small entropy release of about $0.05R\ln 2/\mathrm{Cu}$. Below 6.5 K, the static long-range order transforms abruptly into a metastable state with nearly complete depolarization of muon spins which suggests strong fluctuation. The system then enters a state in which partial long-range order and spin fluctuation coexist down to the lowest experimentally attainable temperature of 20 mK. This work presents a novel system for studying geometric frustration.

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Geometrically frustrated magnetic materials have been of intense recent interest because of their diverse exotic ground states. These include noncollinear antiferromagnetic Néel states in a stacked triangular lattice $R\mathrm{MnO}_3$ (where R is rare earth) [1,2], disordered cooperative paramagnetic states and spin liquid states (in the stacked triangular lattice $CsCoBr_3$ [3], kagomélike $SrCr_4Ga_8O_{19}$ etc., [4–6], pyrochlores $Tb_2Ti_2O_7$ and $Yb_2Ti_2O_7$ [7,8]), spin glasslike states in the absence of chemical disorder (in honeycomb Li_4MgReO_6 [9], pyrochlore $Y_2Mo_2O_7$, and $Dy_2Ti_2O_7$ [10,11]), and materials with icelike spin order and large zero-point entropy such as pyrochlore $Ho_2Ti_2O_7$ [12] and $Dy_2Ti_2O_7$ [13].

Recently, we noted that a cuprate mineral clinoatacamite, $Cu_2Cl(OH)_3$, has the structural feature of corner-sharing tetrahedrons of the Cu^{2+} spins similar to that of pyrochlores [14]. A small antiferromagneticlike change in the temperature dependence of magnetic susceptibility at 18.1 K was observed along with specific heat anomaly with a small entropy fall of 0.05 $R\ln 2$ per Cu^{2+} spin (Fig. 1). A Curie-Weiss temperature of about 190 K was obtained from the temperature dependence of the reciprocal susceptibility with a large ratio of the Curie-Weiss temperature to the transition temperature, suggesting magnetic frustration. Furthermore, anomalies were seen in both specific heat (Fig. 1) and ac susceptibility at 6.4 and 6.2 K, below which demagnetization under a zero field was observed [14]. The magnetic freezing is unusual in that the freezing temperatures are insensitive to the magnetic-field frequency and increase with an applied dc field, and sharp λ-like specific heat anomaly exists in the absence of any change in the crystal lattice.

Herein, we report unusual successive magnetic transitions in clinoatacamite. Muon spin rotation and relaxation (μSR) experiments were carried out on randomly-oriented polycrystalline clinoatacamite using a surface muon beam at TRIUMF (Canada) with a conventional He gas flow cryostat (> 2 K). Additional measurements were performed at KEK (Japan) using a dilution refrigerator (20 mK–2 K). The positive muon beam, polarized to the beam direction, is stopped in a specimen in zero-field (ZF) and longitudinal field (LF) measurements. The time histograms of muon decay positrons are recorded by forward (F) and backward (B) counters as a function of resident time for each μ^+ within the specimen. A positron is emitted preferentially toward the muon spin direction.

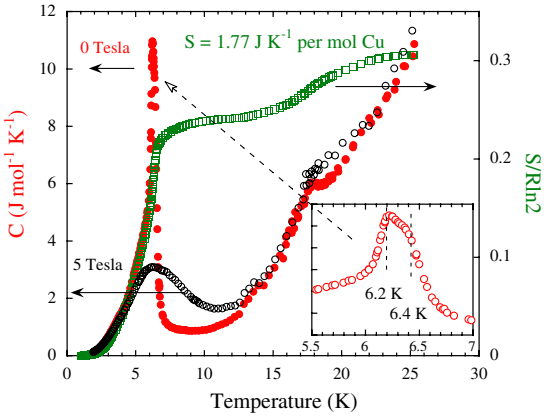

FIG. 1 (color online). The specific heat per mol formula of clinoatacamite $Cu_2Cl(OH)_3$ at ZF (filled circles) and 5 T (open circles), and entropy per mol Cu spin (open squares). The inset is an enlarged view of two anomalies at 6.2 and 6.4 K.

Therefore, asymmetry $a(t) = [F(t) - B(t)]/[F(t) + B(t)]$ of the two histograms (after correction for solid-angle effects) reflects the time evolution of muon spin polarization in the specimen.

In a magnetically ordered phase, the local field of ordered electron spins depolarizes the initially polarized muon spins. In a polycrystalline (i.e., randomly oriented) specimen, $1/3$ of the muon spins have an initial direction parallel to the internal field; $2/3$ of them that are vertical to the field rotate and quickly lose their polarization. The relaxation of the asymmetry is accounted by the sum of an exponential function and a damped oscillation (or many if many muon sites exist) such that

$$a(t) = a_0\left[\frac{1}{3}e^{-\Lambda t} + \frac{2}{3}e^{-\lambda t}\cos(\omega t + \phi)\right], \qquad (1)$$

where longitudinal fields arising from spin fluctuation relax the $1/3$ muon spins and $2/3$ damping reflects the transverse field relaxation. Therefore, $\Lambda = T_1^{-1}$, meanwhile λ includes additional spin-spin relaxation T_2^{-1}. The rotation frequency follows $\omega = \gamma_\mu B_{\text{local}}$ with $\gamma_\mu = 2\pi \times 135.54$ MHz/T. When the magnetic order is in a long-range manner, the damped rotations of the muon spins with time around the baseline of $1/3$ are directly visible.

Transition into a long-range magnetic order below 18.1 K was verified by the beginning of muon spin rotation. Figure 2(a) shows the short-term ($t < 1$ μs) asymmetries (hereafter the polarization of $a(t)/a_0$ is used instead) at typical temperatures. The spectra are well fitted by three distinct frequencies corresponding to three stopping sites for muons (Fig. 3). An antiparallel "up-down" spin arrangement cannot be satisfied for the Cu^{2+} spins with tetrahedral coordination in clinoatacamite. However, a noncollinear arrangement with four apical spins pointing to the center of the tetrahedron can ensure a Néel ground state, as is the case in triangular lattice $R\text{MnO}_3$ [1,2]. Depolarization of the muon spins to a baseline around $1/3$ suggests that the whole sample is long-range ordered. Low values of the muon spin rotation frequencies (e.g., 5.6, 6.8, and 9.1 MHz with respective amplitudes of 0.26, 0.39, and 0.35 at 7 K) in clinoatacamite demonstrate small static fields of 400–700 G. This fact is apparent through comparison with its polymorphous structure of botallackite $Cu_2Cl(OH)_3$ [15]. Assuming that the stopping sites of the positive muons are near the oxygen, the electronic moment involved is roughly estimated as around $0.2\,\mu_B$. The weak internal field and the small entropy reduction ($0.05\,R\ln 2$) across the transition at 18.1 K imply that only a small part of the degree of spin freedom is frozen.

However, the rotations that demonstrating a long-range order begin to disappear near 5.7 K. In addition, the polarization quickly drops to nearly zero at $t = 0.055$ μs [Fig. 2(a)]. Both the rotation and the baseline of polarization recover at further lowered temperatures. The oscillation in the spectrum at 2 K shows that the Cu spins are again magnetically ordered in a long-range manner. However, a complete recovery of the long-range order did not occur, as is apparent from comparison of the rotation spectra at 7 and 2 K, as well as the incomplete recovery of the baseline (about 70% of $1/3$), which we found to be an effective indicator of the incomplete order (Fig. 3). An additional low-temperature experiment confirmed incomplete recovery down to 20 mK.

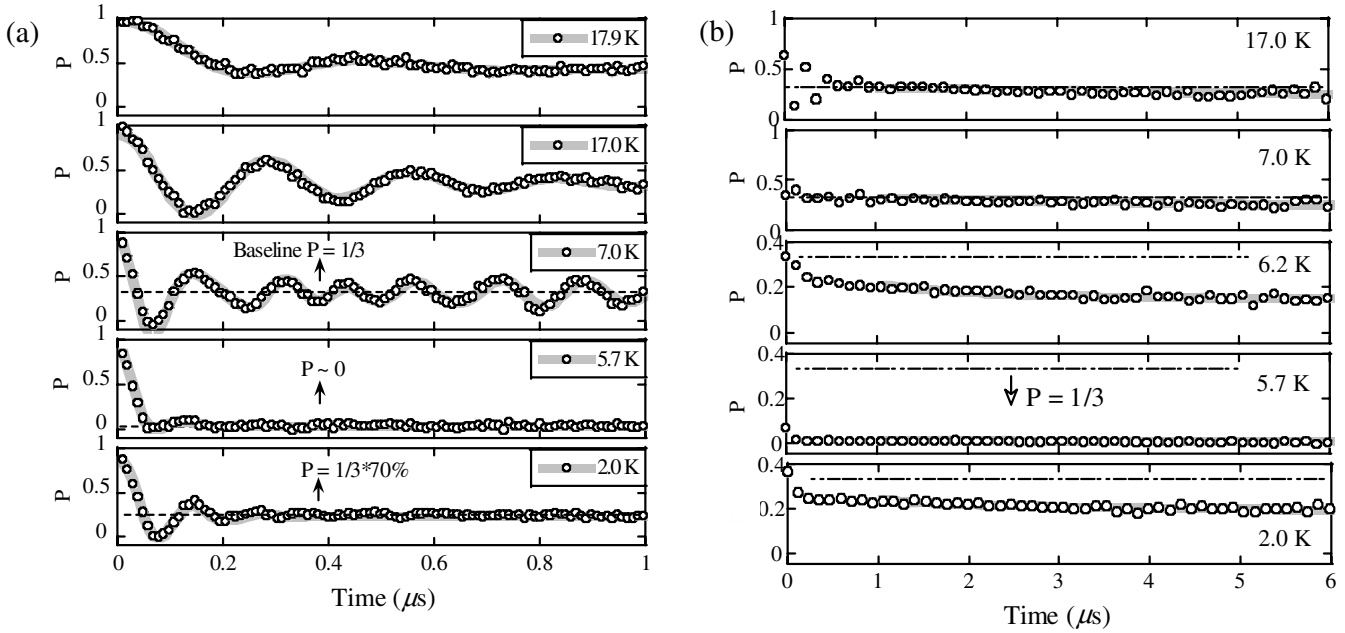

FIG. 2. Depolarization of muon spins at typical temperatures. (a) short-term spectra; and (b) long-term spectra. The broad gray lines are fitted curves. For a clear view, the oscillations of the fitted curves in (b) for $t < 1$ μs are omitted.

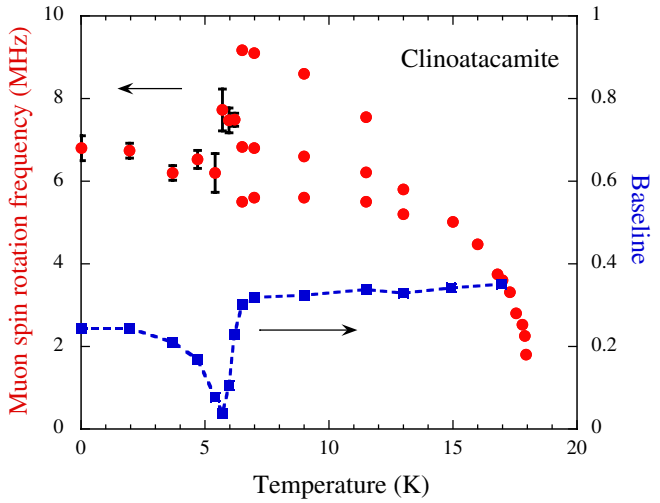

FIG. 3 (color online). Phase diagram for the magnetic transitions in clinoatacamite (the lower part depicts the rapid decrease of the baseline of the polarization spectra around 5.7 K).

Long-term spectra extending to $t = 6$ μs in Fig. 2(b) show that even in the complete long-range order ($7\ \mathrm{K} < T < 17\ \mathrm{K}$), the baseline decreases slightly with a slow relaxation [small Λ in Eq. (1), hereafter denoted as Λ_S], which indicates a small spin fluctuation. On the other hand, the $t < 1$ μs part for $T < 6.5$ K suggests a quick relaxation of the 1/3 component. Because the damping of the 1/3 component for $T < 6.5$ K cannot be fitted with either a single Λ nor a simple distribution function of $1/3\exp[-(\Lambda t)^{\beta}]$, we use two depolarization rates, denoted, respectively, by Λ_S and Λ_Q, to fit the slow relaxation and quick relaxation for the 1/3 component in Eq. (2), as

$$a(t) = a_0\left\{\frac{1}{3}[P_S e^{-\Lambda_S t} + (1 - P_S)e^{-\Lambda_Q t}] + \frac{2}{3}e^{-\lambda t}\cos(\omega t + \phi)\right\}. \quad (2)$$

The slow relaxation Λ_S shows a sharp peak around 5.7 K; meanwhile, its proportion P_S shows a marked decrease [Fig. 4(a)]. At lower temperatures, P_S shows a partial recovery toward 70% that is similar to the change of the baseline. At 2 K, Λ_S shows a similar value (0.03 μs^{-1}) to that in the high-temperature phase. These results demonstrate that the slow Λ_S represents a slow spin fluctuation of the long-range ordered part. The quick relaxation Λ_Q and the transverse field relaxation λ from the short-term spectra are plotted in Fig. 4(b). Both Λ_Q and λ show similar behavior at 5.7 K and a gradual decrease thereafter. At the lowest temperature (2 K as well as 20 mK), depolarization that is attributable to rapid relaxation must be assumed to account for the missing 30% of 1/3, indicating the coexistence of a long-range order and quick spin fluctuation.

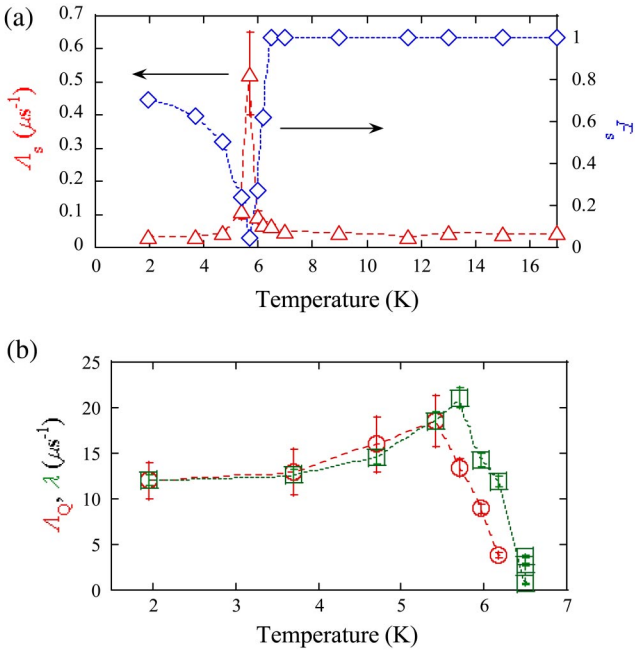

FIG. 4 (color online). (a) Temperature dependence of a slow relaxation Λ_S (open triangles) and its proportion P_S (open diamonds). (b) Temperature dependence of rapid relaxation Λ_Q (open circles) and the transverse field relaxation λ (open squares).

The slow relaxation Λ_S is not decoupled by a longitudinal external field (Fig. 5), which proves the slow spin dynamics for the long-range order. However, an external static field decouples the quick initial drop in the spectra. The latter would be, on the opposite, reminiscent of a static internal field for the quick relaxation. Magnetic susceptibility exhibited a rapid paramagnetic increase below 7 K, then demagnetization in ZF occurred at 6.4 and 6.2 K [14]. The present ZF μSR shows that the paramagnetic behaviors below 7 K occur with a transition from the long-range ordered antiferromagnetic state for $7\ \mathrm{K} < T < 18.1$ K into a rapidly fluctuating state that exists to 5.7 K. Magnetic "freezing" in zero field, as indicated by ac susceptibilities and specific heat near 6.4 and 6.2 K, is witnessed by freezing of the rapidly fluctuating spins, as viewed in Λ_S and Λ_Q in μSR near 5.7 K. Thereafter, the system enters a mixed state of long-range order and dynamic fluctuations (Λ_Q is smaller but still large) at lower temperatures.

The ac susceptibility anomalies at 6.4 and 6.2 K moved to higher temperatures under a dc field [14]. Moreover, they quickly blurred under an increased dc field, and the onset of the specific heat peak broadened to higher temperatures. These facts suggest that the transition from the intermediate metastable state to the low-temperature order is promoted in an applied field. Such an image explains the result of Fig. 5: the decoupling of rapid relaxation by external field is brought about by suppression of rapid dynamic fluctuation of the Cu^{2+} spins, i.e., the external

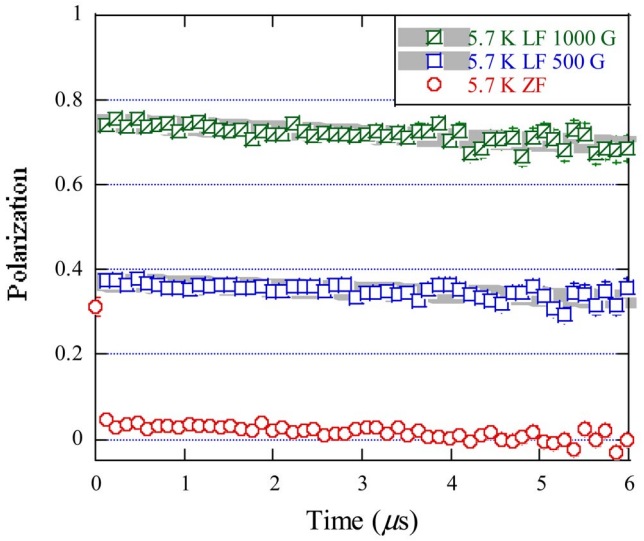

FIG. 5 (color online). Longitudinal field μSR at 5.7 K [thick solid lines are fitted curves using Eq. (3)].

field transforms the dynamic internal field into a static one, and it subsequently decouples the local-static-field-depolarized muon spins. We have fitted the LF-μSR spectra with a well-known formula for polarization in the case of a quasistatic local field under an applied external field to further assess this assumption. The spectra under 1000 and 500 G are well fitted by a modified version of Eq. (1), in which the $1/3$ component in the equation is replaced by $P_Z(x)\exp[-\Lambda_Z(x)]$:

$$P_Z(x) = \frac{3}{4} - \frac{1}{4x^2} + \frac{(x^2-1)^2}{16x^3}\log\frac{(x+1)^2}{(x-1)^2}, \qquad (3)$$
$$\Lambda_Z(x) = [1 - P_Z(x)]\Lambda_0,$$

where x denotes the ratio of the external field versus the local field, i.e., $x = B_L/B_{local}$, and $1/\Lambda_0$ is the correlation time of field. Fitting of the spectra at 500 and 1000 G produced a similar Λ_0 around 0.037 μs^{-1}, which approximates the slow-fluctuation values of Λ_S in the long-range order and reinforces the present scenario.

In the conventional geometric frustrated system of rare-earth pyrochlores, partial disorder has been recently suggested for $Gd_2Ti_2O_7$ by neutron diffraction [16]. Two recent μSR studies on $Gd_2Sn_2O_7$ and $Er_2Ti_2O_7$ respectively, suggested coexistence of static order and spin fluctuation [17,18].

Clinoatacamite is a new geometric frustration system with d-electron spins. Temperature-driven successive phase transitions from a noncollinear Néel state into rapid spin-fluctuation and further into coexisting long-range order and fluctuation in clinoatacamite outline a system to study these exotic quantum effects in one regularly ordered compound. The order-to-disorder transition at lowered temperatures is also unusual. The magnetic dynamics in this transition metal d-electron system should be easier to model theoretically than the rare-earth f electrons in pyrochlores.

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