Low-temperature magnetization of the low-dimensional magnet Cu$_3$Mo$_2$O$_9$ under high magnetic fields

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Abstract. We report the magnetization curve under magnetic fields $H$ up to 30 T at low temperatures in a tetrahedral spin-chain system Cu$_3$Mo$_2$O$_9$ single crystal. This material shows successive phase transitions to an antiferromagnetic phase at $T_N = 7.9$ K and a weak ferromagnetic (WF) phase at $T_c \simeq 2.5$ K in low magnetic fields. As the magnetic field increases below $T_N$, two rapid increases in magnetization occur at $0 \sim 0.1$ and 19.3 T for $H/a$ and 0.3 \sim 0.8 and 17.5 T for $H/c$. However, these increases do not occur for $H/b$. These facts refute the conventional spin flop transition. The rapid increases disappear above $T_N$. The magnetic moments are canted toward the $ac$ plane by the Dzyaloshinskii-Moriya interaction in the WF phase. Consequently, these rapid increases in magnetization at high magnetic fields are interpreted by sudden rotations of the WF moments around the $b$ axis.

1. Introduction

Applying a magnetic field, $H$, induces intriguing phenomena in one-dimensional quantum spin systems possessing frustration and competition among the exchange interactions in strong spin fluctuations. One of the phenomena is topological quantization of a physical quantity when a magnetic field is applied, and this phenomenon is called the magnetization plateau. In a frustrated diamond-chain system, Cu$_3$(CO$_3$)$_2$(OH)$_2$, a 1/3 magnetization plateau was found between 11 and 30 T [1]. Meanwhile, in a quasi-one-dimensional spin system, BaCu$_2$Si$_2$O$_7$, where the Dzyaloshinskii-Moriya (DM) exchange and interchain interactions are competing, two-stage spin-flop transitions occurred successively at $H = 2.0$ and 4.9 T [2].

Recently, we found successive phase transitions in a tetrahedral spin-chain system, Cu$_3$Mo$_2$O$_9$ [3]. The magnetic susceptibility and magnetization curve along the $a$ and $c$ axes show weak ferromagnetic-like behavior below an antiferromagnetic (AF) second-order phase transition at $T_N = 7.9$ K in low magnetic fields (below 5 T), whereas we observed that it does not occur along the $b$ axis. Moreover, a weak ferromagnetic (WF) phase transition occurs at $T_c \simeq 2.5$ K. These phenomena are explainable by both magnetic frustration among symmetric exchange interactions and competition between symmetric and asymmetric Dzyaloshinskii-Moriya (DM) exchange interactions [3].

As shown in Fig. 1(a), Cu$_3$Mo$_2$O$_9$ has three crystallographically inequivalent Cu$^{2+}$ sites (Cu1, Cu2 and Cu3), and they uniformly form alternating tetrahedra along the $b$ axis. The spin system can be roughly treated as a composition of spin-1/2 AF uniform chains and AF dimers.
On the basis of the results for antiferromagnets such as Cu$_2$Fe$_2$Ge$_4$O$_{13}$ [4, 5] and Cu$_2$CdB$_2$O$_6$ [6], we inferred that a spin-singlet-like pair of spins on Cu2 and Cu3 sites is formed and that the magnetic moments are not zero even at low temperatures because of interactions with Cu1 spins. The magnetic frustration between the two spins on the neighboring Cu1 sites is generated with Cu2 or Cu3 because they form a triangle and interact with one another.

In this paper, we report the magnetization curve under magnetic fields up to 30 T in a Cu$_3$Mo$_2$O$_9$ single crystal below about 10 K. The high magnetic field can be obtained when the hybrid and/or pulsed magnets are used. Using a hybrid magnet, we measured the magnetization up to 30 T and found two successive anomalous rapid increases in magnetization in a Cu$_3$Mo$_2$O$_9$ single crystal for $H//a$ and $H//c$. We discuss this strange magnetic behavior.

2. Experiment

Single crystals of Cu$_3$Mo$_2$O$_9$ were prepared using a flux method [3]. The magnetization measurements along the $a$, $b$ and $c$ axes were carried out with an extraction-type magnetometer when high magnetic fields were applied up to $H = 30$ T using a hybrid magnet, which consists of a water-cooled magnet with an outer superconducting magnet, at the Tsukuba Magnet Laboratory in the National Institute for Materials Science (NIMS). The magnetic susceptibility $M/H$ and magnetization $M(H)$ below 5 T were also measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS XL5).

3. Results and Discussion

The inset of Fig. 2 shows the temperature dependence of the magnetic susceptibility at $H = 0.1$ T below 15 K, which was obtained using a SQUID magnetometer. An increase was observed in the susceptibility along the $a$ axis as the temperature decreased below $T_N = 7.9$ K, indicating an AF phase transition. Figure 2 shows the magnetization as a function of the magnetic field at 2.0 K up to 30 T in logarithmic scales. The magnetization curves $M_a(H)$ and $M_c(H)$ rapidly increase at 0–0.1 and 19.3 T for $H//a$ and 0.3–0.8 and 17.5 T for $H//c$, respectively. However, these rapid increases were not observed for $H//b$. These facts refute the conventional spin flop...
transition because the spins are directed approximately to the $b$ axis below $T_N$. The rapid increases in higher fields for $H//a$ and $H//c$ will be discussed later. As reported in Ref. [3], the rapid increase in the lower field is interpreted in terms of an arrangement of the WF moments on a linear spin chain. As shown in Fig. 1(b), two kinds of spin ordering, cases 1 and 2, are formed in a chain. When all the WF moments in all the chains fall into case 1 or 2, the total magnetic moment of the system has only the $a$ component, and the WF long-range order parallel to the $a$ axis is realized, as shown in Fig. 1(c). In a similar way, when all the WF moments in the $\beta$ chains fall into case 1 and those in the $\alpha$ chains fall into case 2, or vice versa, the total magnetic moment of the system has only the $c$ component. The latter is achieved when the magnetic field above 0.3 T is applied parallel to the $c$ axis. These spin alignments are achieved below the magnetic fields where the magnetization curves rapidly increase, i.e., below 17.5 T for $H//c$ and below 19.3 T for $H//a$.

Figure 3 shows the magnetization as a function of magnetic field up to 30 T at 2.0, 4.3, 6.0 and 10.4 K in linear scales. Only the magnetization curves in the field-increasing process are drawn in the figure because no magnetic hysteresis was observed above 2 T. As shown in Fig. 2, the $M_a(H)$ rises almost linearly between $H = 6$ and 18.5 T and agrees with $M_b(H)$ and
$M_c(H)$. Between 18.5 and 20 T, the $M_a(H)$ increases rapidly without magnetic hysteresis, and the magnetic field at the jump is defined as $H_j = 19.3$ T for $H//a$, which is the mean value between them. Above 20 T, the $M_a(H)$ rises linearly again, but the gradient of the $M_a(H)$ between $H = 20$ and $30$ T is steeper than that between $H = 6$ and 18.5 T. Similarly, the jump in $M_c(H)$ occurs between $H = 17$ and 18 T, and then we obtain $H_j = 17.5$ T for $H//c$. The magnitude of $M_a(H)$ at 20 T is 0.13 $\mu_B$/Cu, which is nearly equal to 1/4 of the full moment. However, the jump in magnetization cannot be interpreted in terms of the 1/4 magnetization plateau because the three crystallographically inequivalent Cu$^{2+}$ ions (Cu1, Cu2 and Cu3) have spin-1/2 magnetic moment. These jumps in the magnetization also occur at 4.3 K in the same magnetic fields $H_j$. Bends in the magnetization occur at 6.0 K in almost the same magnetic fields $H_j$ for $H//a$ and $H//c$. These bends suggest that the magnetization jumps broaden. When the temperature rises to 10.4 K, which is above $T_N$, the jumps do not occur. As a result, these jumps may be related to the AF long-range order.

Let us now consider the origin of the jump in magnetization at high magnetic fields. The jumps occurred when the magnetic fields $H_j$ correspond to 13.7 and 12.8 K for $H//a$ and $H//c$, which are roughly equal to the DM interaction energy ($=20.8$ K). Here the $g$ factor is given as $(g_a, g_b, g_c) = (2.090, 2.193, 2.180)$ [3]. This fact suggests that the inclination of spins from the $b$ axis by the DM interaction is an origin of the jump in magnetization. At present, we think that it originates from the rotation of the WF moment. All the WF moments rotate suddenly toward the direction of the applied magnetic field on the $ac$ plane in the jumps. The height of the jump is approximately 0.03 $\mu_B$/Cu for both $H//a$ and $H//c$. Taking the low-field magnetization results below 2 T into account, the magnetic moment is canted from the $b$ axis at 2.38°, and the component of the WF moment has angles of $\pm 23.4°$ from the $c$ axis [3], which is induced by the DM interaction, as shown in Fig. 1. Therefore, the WF moment $M_{WF}$ is given as $M_{WF} = 6.9 \times 10^{-4} \mu_B$/Cu, which is much smaller than the height of the jump, 0.03 $\mu_B$/Cu. However, the canted angle increases gradually as the magnetic field increases, and the magnetic moments move toward the direction of the applied magnetic fields. A sudden rotation of the WF moments probably occurs when the magnetic field overcomes the DM interaction.

The exotic jump in magnetization for the magnetic hard axes has not yet been fully understood. However, such a one-dimensional frustrated quantum spin system as Cu$_3$Mo$_2$O$_9$ is very susceptible to various external perturbation, and our finding is a good example to demonstrate the rich physics of one-dimensional frustrated quantum spin systems.

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