Studies of magnetization plateau in two cuprates

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Abstract. We report magnetism of Cu$_2$CdB$_2$O$_6$ and Cu$_3$(P$_2$O$_6$OH)$_2$ that show a magnetization plateau. In Cu$_2$CdB$_2$O$_6$, a 1/2 magnetization plateau in magnetic fields above 23 T and antiferromagnetic (AF) long-range order (AFLRO) in low fields were observed. There are two kinds of Cu sites [Cu(1) and Cu(2)], which are located adjacent to each other. Spins on the Cu(1) and Cu(2) sites are in a nearly spin-singlet state and form AFLRO, respectively, although interactions between the Cu(1) and Cu(2) spins cannot be ignored. Cu$_2$CdB$_2$O$_6$ is the first material that shows such coexistence in an atomic scale. In Cu$_3$(P$_2$O$_6$OH)$_2$, a spin-1/2 threefold-period chain with $J_1$-$J_2$ interactions exists, where $J_1$ and $J_2$ denote two AF exchange interaction parameters. A 1/3 magnetization plateau was observed above 12 T. Cu$_3$(P$_2$O$_6$OH)$_2$ is the first model compound of AF threefold-period chains showing a magnetization plateau.

1. Introduction

Low-dimensional quantum spin systems exhibit various interesting phenomena. One example is an energy gap between ground and excited states seen in some spin systems such as the spin-Peierls system [1]. If the ground state is nonmagnetic, existence of the energy gap can be confirmed by magnetic susceptibility that decreases rapidly on cooling at low temperatures. On the contrary, if the ground state is magnetic, we cannot determine whether the energy gap exists or not from magnetic susceptibility. A magnetization plateau can appear in situation that some spins are in a nearly spin-singlet state with the energy gap and that the other spins are almost polarized parallel to the applied field. Thus, in some spin systems, we can conclude existence of the energy gap from observation of the magnetization plateau. Consequently, the magnetization plateau has become one of hot topics in high magnetic field studies [2]. Recently, we have found two cuprates Cu$_2$CdB$_2$O$_6$ and Cu$_3$(P$_2$O$_6$OH)$_2$ that have the magnetization plateau and magnetic ground state in total, and report our results.

In the two cuprates, all Cu ions are divalent and have spin-1/2. The inset of Fig. 1(a) shows schematically Cu positions in Cu$_2$CdB$_2$O$_6$. Two crystallographic Cu sites [Cu(1) and Cu(2)] exist along with five kinds of short Cu-Cu bonds (bonds 1 to 5) whose Cu-Cu distances are 0.298 to 0.356 nm. Signs of exchange interaction parameters ($J_1$, $J_2$, and $J_3$) in three kinds of Cu-Cu bonds (bonds 1 to 3) are presumed to be antiferromagnetic (AF) from Cu-O-Cu angles (99.24, 118.48, and 102.39 degrees, respectively). In bonds 4 and 5 (not shown), no neighboring oxygen site exists to which both two Cu sites in each bond are connected. For that reason, exchange interactions in these bonds are expected to be smaller than $J_1$, $J_2$, or $J_3$. In addition, Cu-Cu distances in the other bonds are larger than 0.464 nm. Consequently, Cu$_2$CdB$_2$O$_6$ is probably a compound including a unique spin system formed by $J_1$, $J_2$, and $J_3$ represented in Fig. 1(a). The inset of Fig. 2(a) shows schematically positions of Cu and O connecting to Cu in Cu$_3$(P$_2$O$_6$OH)$_2$. Two crystallographic Cu sites [Cu(1) and Cu(2)] exist along with
Figure 1 (a) Magnetic susceptibility $\chi$ of Cu$_2$CdB$_2$O$_6$ (solid curve) and the QMC result (dashed curve) for the expected spin system shown in the inset with $J_1 = 160$ K, $J_2 = 38.8$ K, and $J_3 = 9.7$ K. The interaction parameter $J_i$ is defined in the Hamiltonian $H = \sum_{\langle i,j \rangle} J_i S_i S_j$. (b) Magnetization $M$ of Cu$_2$CdB$_2$O$_6$ at 2.9 K (solid curve). Diamonds, circles, and squares respectively indicate the QMC results of $M$ for total, Cu(1), and Cu(2) spins. The magnetization is expressed as a spin value $S = M/\mu_B N_A$, where $g$, $\mu_B$, and $N_A$ are the $g$ value of Cu$^{2+}$, Bohr magneton, and Avogadro's constant, respectively. We determined $g = 2.10$ in an electron spin resonance (ESR) measurement at room temperature. The left and right inset figures show the spin states in low $H$ and plateau region, respectively. The ellipse and arrow represent the nearly spin-singlet pair and Cu(2) spin.

two kinds of short Cu-Cu bonds. Distances of Cu-Cu in the first-shortest and second-shortest bonds (bonds 1 and 2), which are indicated respectively by solid and dotted bars, are 0.306 and 0.328 nm. The bond 1 has two identical Cu-O-Cu paths whose angle is 100.8 degrees. The bond 2 has two Cu-O-Cu paths, but they differ slightly from each other. Angles in the two paths are 98.0 and 98.5 degrees. From the Cu-Cu distances and Cu-O-Cu angles, AF exchange interactions are expected to exist in the Cu paths, but they differ slightly from each other. Angles in the two paths are 98.0 and 98.5 degrees. Therefore, exchange interactions in these bonds are expected to be smaller than $J_1$ and $J_2$. Consequently, Cu$_3$((P$_2$O$_6$OH)$_2$ is probably a compound including the spin-1/2 threefold-period ($J_1$-$J_2$-$J_3$) chain.

2. Methods of experiments and calculation

We synthesized Cu$_2$CdB$_2$O$_6$ powder by solid-state reaction method and Cu$_3$((P$_2$O$_6$OH)$_2$ powder from a mixture of 0.5 g of CuO and 20 mL of H$_3$PO$_4$. We measured magnetizations up to 5 T and 30 T using a superconducting quantum interference device (SQUID) magnetometer and an extraction-type magnetometer in a hybrid magnet at the High Magnetic Field Center, NIMS, respectively. We calculated the susceptibility and magnetization by quantum Monte Carlo (QMC) techniques using the loop algorithm and using the directed-loop algorithm in the path-integral formulation, respectively. The numbers of Cu sites in the QMC simulations are 1,000 and 360 for Cu$_2$CdB$_2$O$_6$ and Cu$_3$((P$_2$O$_6$OH)$_2$. We have performed more than one million updates. Finite-size effects and statistical errors are negligible in the scale of figures represented in this paper.

3. Cu$_2$CdB$_2$O$_6$

The solid curve in Fig. 1(a) represents the temperature $T$ dependence of magnetic susceptibility $\chi$ of Cu$_2$CdB$_2$O$_6$ in the magnetic field of $H = 0.1$ T. The susceptibility of Cu$_2$CdB$_2$O$_6$ has a maximum around 11 K and seems to reach a finite value at 0 K. We observed a $\lambda$-type behavior around 10 K in $d\chi/dT$ and a peak at 9.8 K in the specific heat (not shown). Taking the expected signs of the exchange interactions into account, AF long-range order (AFLRO) probably appears at $T_N = 9.8$ K. The solid curve in Fig. 1(b) represents the $H$ dependence of the magnetization $M$ at 2.9 K. The most prominent feature is a 1/2 magnetization plateau above 23 T. The dashed curve in Fig. 1(a) shows the QMC result of $\chi$ for the spin system in Fig. 1(a) with $J_1 = 160$ K, $J_2 = 38.8$ K, and $J_3 = 9.7$ K, and agrees with the experimental $\chi$. Diamonds represent the QMC result of $M$ at 2.9 K for the same model and can reproduce well the experimental $M$. Therefore, the spin system in Fig. 1(a) can explain the magnetic
properties of Cu$_2$CdB$_2$O$_6$ at least as the first approximation. As mentioned above, however, AFLRO appears at low $T$, which is caused by weak three-dimensional (3D) couplings ignored in the spin model. The discrepancy between experimental and calculated $\chi$ at low $T$ is due to the appearance of AFLRO.

Spin states can be understood as follows [Fig. 1(b)]. The appearance of the 1/2 magnetization plateau means that half of spins are in a nearly spin-singlet state with a dimer gap, which corresponds to the magnetic field to break the nearly spin-singlet state, and that the other spins are almost polarized parallel to the applied field. Therefore, the magnetization cannot increase in the plateau region with an increase in the magnetic field. The QMC results in Fig. 1(b) show that moments of the Cu(1) spins (open circles) are very small in the low-field regime, indicating that the Cu(1) spins form nearly singlet pairs with the dimer gap below an end field of the plateau. The magnetization starts to increase again around 108 T (not shown), which means that a value of the dimer gap is about 152 K for $g = 2.10$. The dimer gap corresponds to binding energy of singlet pairs and is mainly determined by the Cu(1) spin interaction. Thus, the value of the dimer gap (152 K) is close to $J_1$ (160 K). The QMC results in Fig. 1(b) show that moments of the Cu(2) spins (open squares) are almost polarized in the plateau region.

A value of an effective interaction between two Cu(2) spins through the AF dimer formed by the Cu(1) spins is roughly estimated as $J_{12} = J_1^2/J_1 = 9.4$ K. Because the values of $J_{12}$ and $J_1$ are not so large, the Cu(2) spins can be almost saturated above 23 T in spite of the large values of $J_1$ and $J_2$. AFLRO can appear in the Cu(2) spins by this effective interaction, the $J_1$ interaction, and other weak 3D interactions which are omitted in our model. The distance of the nearest-neighbor Cu(1)-Cu(2) bond (the bond 2) is only 0.322 nm and the interaction in this bond (38.8 K) cannot be ignored in comparison with other interactions. Nevertheless, the coexistence of the nearly singlet state of the Cu(1) spins and AFLRO of the Cu(2) spins appears. We can say that this is "coexistence in an atomic scale" and such coexistence in quantum spin systems has not been found before the present study.

4. Cu$_3$(P$_2$O$_6$OH)$_2$

The solid curve in Fig. 2(a) shows the $T$ dependence of $\chi$ measured in $H = 0.1$ T. On cooling, the susceptibility increases following the Curie-Weiss law from 300 K, shows weak temperature dependence around 40 K, increases rapidly below about 20 K, and has a maximum around $T_{\text{max}} = 3$ K. We measured the specific heat and did not observe magnetic long-range order above 2 K (not shown). Thus, the maximum of $\chi$ around 3 K indicates development of AF short-range correlation. The solid curve in Fig. 2(b) indicates the $H$ dependence of $M$ at 1.6 K. The most prominent feature is a 1/3 magnetization plateau above 12 T. According to the theorem in [5], magnetization curves at 0 K in quantum spin chains might have plateaus at $m'$ that satisfies the formula of $n(S'-m') = \text{integer}$. Here, $n$ is the period of the ground state; $S'$ and $m'$ respectively represent the total spin and magnetization per unit cell. Because $n = 3$ and $S' = 1/2$ in the spin-1/2 threefold-period chain, the magnetization plateau can appear at $m' = 1/6$ which means the 1/3 magnetization plateau. Thus, the 1/3 magnetization plateau
in Cu₃(P₂O₆OH)₂ is consistent with the theorem in [5]. The dashed curve labeled by squares in Fig. 2(a) shows the QMC result of χ for the spin-1/2 threefold-period chain with J₁ = 95 K and J₂ = 28 K, and overlaps with the experimental χ. The dashed curve indicated by ‘total’ in Fig. 2(b) represents QMC results of M for the same model and is consistent with the experimental magnetization except for slight discrepancy around 10 T. Consequently, the spin-1/2 threefold-period chain with J₁ = 95 K and J₂ = 28 K can explain magnetic properties of Cu₃(P₂O₆OH)₂.

Figure 2(a) shows the QMC results of χ for the total, Cu(1), and Cu(2) spins. The susceptibility of the Cu(2) spins increases with decreasing T from 300 K, shows a maximum at 62 K, and decreases to small values at low T. Because the J₁ interaction is dominant in Cu₃(P₂O₆OH)₂, two Cu(2) spins connected by the J₁ interaction form a state that resembles a spin-singlet pair. Therefore, χ of the Cu(2) spins is similar to χ of an isolated AF dimer. When the exchange interaction is 95 K, χ of an isolated AF dimer has a maximum at 59 K, which is close to Tₘₐₓ = 62 K in χ of the Cu(2) spins. In contrast to χ of an isolated AF dimer, χ of the Cu(2) spins is not negligible at low T because the Cu(1) spins affect the Cu(2) spins through the finite J₂ interaction. The susceptibility of the Cu(1) spins increases with decreasing T from 300 K and shows a maximum at 3 K like low-dimensional antiferromagnets. An effective interaction exists between two Cu(1) spins through the AF dimer formed by the Cu(2) spins and the system consisting of the Cu(1) spins behaves as an effective AF chain. The value of the effective interaction is estimated roughly as Jₑffect = J₂/J₁ = 8 K. The value of Tₘₐₓ is 5 K in an AF uniform chain with exchange interaction of 8 K. It is close to Tₘₐₓ = 3 K in χ of the Cu(1) spins as seen in Fig. 2(a).

Figure 2(b) shows QMC results of M for the total, Cu(1), and Cu(2) spins. As was above-mentioned, because two Cu(2) spins that are connected by the J₁ interaction form a state that resembles a spin-singlet pair, the moment of the Cu(2) spins is small at low H. The moment of the Cu(1) spins, in contrary, is almost saturated in the plateau region because of the small value of Jₑffect = 8 K. The AF uniform chain with exchange interaction of 8 K has a saturation field of 11 T for g = 2.12, which is close to the starting field of the plateau. Finally, we show a value of a gap in the plateau region. The total magnetization starts to increase again around 65 T (not shown), which means that the value of the gap is 92 K for g = 2.12. That gap is determined mainly by the J₁ interaction. Therefore, the gap value is close to J₁ (95 K).

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