Experimental Observation of the 1/3 Magnetization Plateau in the Diamond-Chain Compound $Cu_3(CO_3)_2(OH)_2$

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The magnetic susceptibility, high field magnetization, and specific heat measurements of $Cu_3(CO_3)_2 \times (OH)_2$, which is a model substance for the frustrating diamond spin chain model, have been performed using single crystals. Two broad peaks are observed at around 20 and 5 K in both magnetic susceptibility and specific heat results. The magnetization curve has a clear plateau at one third of the saturation magnetization. The experimental results are examined in terms of theoretical expectations based on exact diagonalization and density matrix renormalization group methods. An origin of magnetic anisotropy is also discussed.

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The physical system is said to be frustrated if its interaction bonds are not satisfied simultaneously and, as a result, the ground state is highly degenerate. The frustration plays an essential role in several physical fields such as magnetism [1], superconductivity [2], and even in a field of neural networks [3]. The frustrated system on a regular lattice, or the geometrically frustrated system, is worthwhile to study, since we can investigate only the frustration effect on the physical properties, not worried by a problem of randomness, which is inevitable in a glass system. One-dimensional (1D) quantum frustrated spin systems have an advantage that the precise comparison is possible between experimental and theoretical results. One of the most important findings in the 1D quantum spin system is a presence of a magnetization plateau in some magnets. In a plateau region, the magnetization keeps constant value in spite of increasing a magnetic field. Oshikawa *et al.* [4] theoretically investigated general Heisenberg chains in a magnetic field to find that the system could have the magnetization plateau if a spin system satisfied a plateau condition $n(S - m) =$ integer, where n, S, and m are the period of the spin state, the magnitude of the spin, and the magnetization per site in the unit of $g\mu_B$, respectively. They claimed that the magnetization plateau is a kind of topological quantization.

One of the simplest 1D quantum frustrated system is a diamond-chain model in which diamond-shaped units compose a one-dimensional lattice [Fig. 1(a)]. Takano *et al.* [5] studied theoretically the ground state of a prototypical diamond chain ($J_1 = J_3$) and Tonegawa *et al.* [6] investigated the ground state of the more general distorted diamond chain in which exchange coupling constants J_1, J_2, and J_3 between adjacent $S = 1/2$ spins are different from each other. They determined the phase diagram at $T = 0$ which is composed of the ferrimagnetic phase, the dimerized (D) phase, and the spin fluid (SF) phase [7,8]. The distorted diamond chain is approximated to be a periodic array of J_2-dimer and monomer spins if $J_2 \gg J_1, J_3$, or alignment of linear trimer spins when $J_1 (\text{or} J_3) \gg J_2$. In these two extreme cases, a 1/3 magnetization plateau is intuitively understood to be present. The ground state magnetization curve for a more general case is calculated numerically by the above authors, and the 1/3 magnetization plateau is found to appear in a broad region of the phase diagram. This 1/3 magnetization plateau in the distorted diamond chain corresponds to $S = 1/2$, $m = 1/6$, and $n = 3$ in the plateau condition.

Experimental work on the magnetic properties of (distorted) diamond chains, however, have not progressed because of a lack of appropriate actual substance. Recently, we have found that a compound $Cu_3(CO_3)_2(OH)_2$ can be regarded as a model substance of distorted diamond chain [9]. In this Letter, we investigate the magnetic properties of $Cu_3(CO_3)_2(OH)_2$ by means of magnetic susceptibility [$\chi(T)$], high field magnetization and specific heat [$C(T)$] measurements, and find the presence of the 1/3 magnetization plateau. The experimental magnetization curve is compared with a calculated one.

The crystal structure of $Cu_3(CO_3)_2(OH)_2$, or the natural mineral name, azurite, has the space group $P2_1/c$ with the lattice constants $a = 501.09$ pm, $b = 584.85$ pm, $c = 1034.5$ pm, and $\beta = 92.43°$ [10]. Monomers and dimers made of Cu^{2+} ions with a localized spin $S = 1/2$ are arranged along the crystallographic b axis to form an infinite chain as shown in Fig. 1(b). A shape formed by exchange coupling bonds between adjacent Cu^{2+} ions via O^{2-} ions

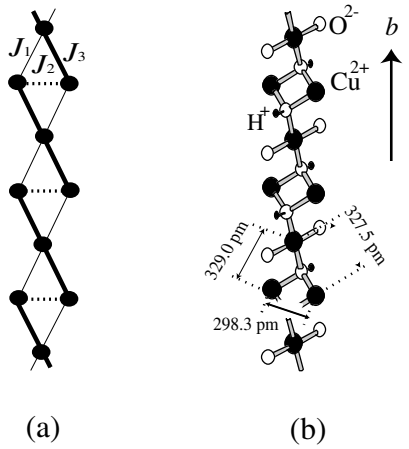

FIG. 1. (a) The distorted diamond chain. Solid circles represent spin 1/2 coupled by exchange interactions J_1, J_2, and J_3. (b) Schematic view of the crystal structure of the azurite $Cu_3(CO_3)_2(OH)_2$ along the b axis.

corresponds to the distorted diamond-chain model. Only a few papers have been reported on the magnetic properties of azurite. A magnetic order is reported to occur at $T_N = 1.86$ K from the magnetic susceptibility [11] and 1.84 K from the specific heat measured between 1.7 and 3.6 K [12]. NMR spectra below 4.2 K are also reported [13].

All measurements in this study are performed using the natural mineral single crystal of $Cu_3(CO_3)_2(OH)_2$ purchased at a stone shop. The powder x-ray diffraction pattern measured with a crashed single crystal indicates a single phase of sample without impurity. The magnetic susceptibility is measured using the Quantum Design PPMS (Physical Properties Measurements System) in the temperature range between 2.0 and 300 K in an applied field of 0.1 T. The high field magnetization curves are measured below 4.2 K up to about 40 T using an induction method in a pulsed magnetic field. The specific heat is measured by the quasiadiabatic method in the temperature region between 0.33 and 200 K.

Figure 2(a) shows the magnetization curves of $Cu_3(CO_3)_2(OH)_2$ with the field applied along b axis (i.e., chain direction). No hysteresis is observed in the magnetization curves for increasing and decreasing fields. Three anomalies are observed at $H_{c1}^{\parallel} = 16$ T, $H_{c2}^{\parallel} = 26$ T, $H_{c3}^{\parallel} = 32.5$ T. These anomalies become more distinct as the temperature is decreased. The magnetization is nearly saturated at $H_{c3}^{\parallel}$ with a saturation magnetization of $M_s = 0.95\mu_B/Cu^{2+}$, which is slightly smaller than the expected value for Cu^{2+} ($S = 1/2$); $g\mu_B S = 1\mu_B$ for $g = 2$. The most important finding in this high field magnetization measurement is that the magnetization in the field range between $H_{c1}^{\parallel}$ and $H_{c2}^{\parallel}$ kept an approximately constant value of $0.3\mu_B$, which is almost 1/3 of M_s. This is the first experimental evidence of the 1/3 magnetization plateau in the distorted diamond spin chain predicted by theoretical studies. The 1/3 plateau is also observed in the magnetization curve for magnetic field perpendicular to the b axis

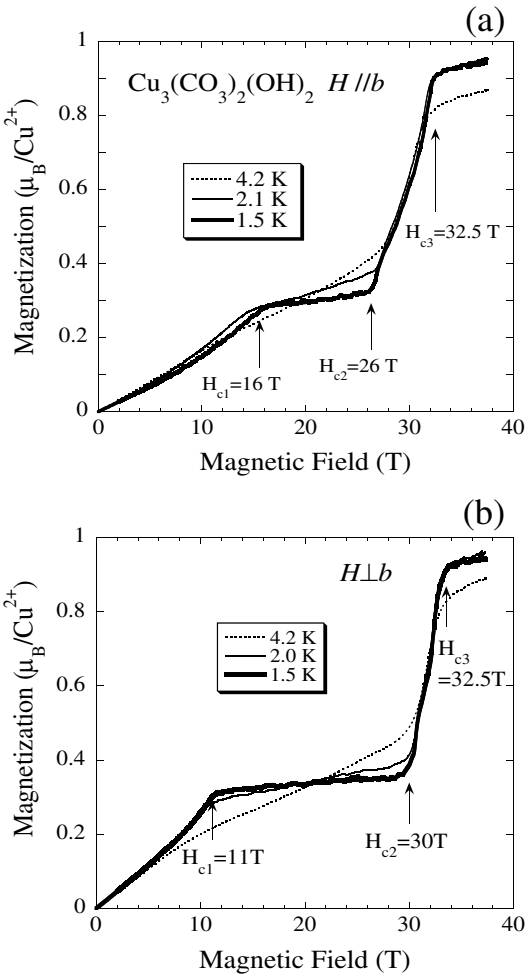

FIG. 2. The high field magnetization curves of $Cu_3(CO_3)_2 \times (OH)_2$ measured below 4.2 K. The magnetic field was applied along the b axis (a) and perpendicular to the b axis (b), respectively.

as shown in Fig. 2(b). The critical fields in this field configuration are $H_{c1}^{\perp} = 11$ T, $H_{c2}^{\perp} = 30$ T, and $H_{c3}^{\perp} = 32.5$ T. The field region of the 1/3 plateau for $H \perp b$ is broader than that for $H \parallel b$, while the saturation field H_{c3} did not change in respect to the field direction. In a lower field region, both magnetizations for $H \parallel b$ and $H \perp b$ increase almost linearly as a function of the magnetic field, indicating an absence of a spin gap in the zero-field ground state.

Figure 3 shows the temperature dependence of the magnetic susceptibilities for $H \parallel b$ and $H \perp b$. The diamagnetic contribution from core electrons is estimated using the Pascal's law [14] and subtracted from the raw data. As temperatures are decreased, rounded peaks are observed at 23 K in both curves. $\chi(T)$ for $H \perp b$ becomes larger than that for $H \parallel b$ below about 20 K. As the temperature is lowered further, second peaks appear at 5 K in both $H \parallel b$ and $H \perp b$ susceptibilities. As a result, the magnetic susceptibility curves of $Cu_3(CO_3)_2(OH)_2$ have turned out to show two round peaks, which are not common in one-dimensional magnets without the spin frustration effect.

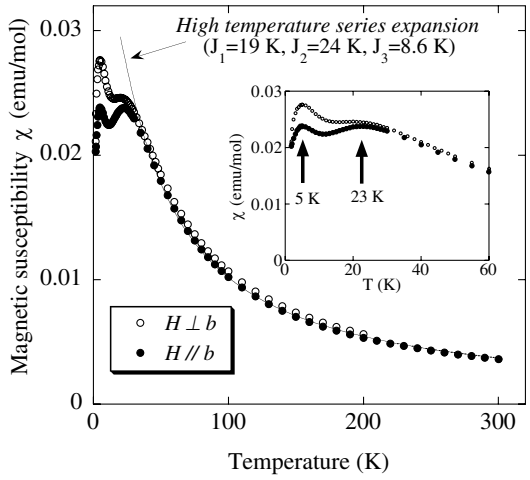

FIG. 3. The temperature dependence of the magnetic susceptibilities for $H \parallel b$ and $H \perp b$. The solid line is the best fitted result of high temperature series calculation using the parameters shown in figure. The inset is the low temperature part of the magnetic susceptibility. The diamagnetic contribution from core electrons is subtracted in this figure.

Figure 4 shows the temperature dependence of the specific heat measured at zero magnetic field. A lattice contribution to the specific heat is not subtracted. A sharp peak is observed at 1.8 K, reflecting the occurrence of the long range magnetic order. This temperature is consistent with the reported value of the Néel temperature. A new finding from our specific heat measurement is the appearance of two rounded peaks at around 4 and 18 K. These temperatures coincide closely with those where the magnetic susceptibilities also show the round peaks.

Now, we are going to analyze our experimental results. We have calculated the magnetization curve at $T = 0$ for the distorted diamond-chain model using the density matrix renormalization group method. The magnetization curves for various interactions ratio are calculated. The best fitting calculation to the experimental result is obtained with the exchange interactions ratio, J_1:J_2:J_3 = 1:1.25:0.45. The calculated result is drawn by a dotted line in Fig. 5 and compared with the experimental curve for $H \parallel b$ at 1.5 K. As the bond length corresponding to J_2 (298.3 pm) is shorter than that for J_1 or J_3 (327.5 pm or 329.0 pm), it is reasonable that J_2 is the strongest interaction in the three exchange parameters. The point corresponding to the ratio of J_1:J_2:J_3 = 1:1.25:0.45 in the phase diagram is close to a phase line separating the D and the SF phases [6]. The spin gap is exactly zero in the SF phase and is almost zero in the D phase very close to the phase line, which is consistent with the experimental finding of the absence of the spin gap. Recent high field ESR measurement also suggests that the ground state of $Cu_3(CO_3)_2 \times (OH)_2$ is the SF phase [15].

In order to determine the absolute value of the exchange coupling constants, we have compared the $\chi(T)$ with a theoretical curve obtained by a high temperature series expansion [16] keeping the coupling ratio as J_1:J_2:J_3 = 1:1.25:0.45. The best fitted result is obtained when the values $J_1 = 19$ K, $J_2 = 24$ K, $J_3 = 8.6$ K are employed. The calculated result is shown by a solid curve in Fig. 3.

Next, let us discuss the origin of the double peaks observed both in the magnetic susceptibility and the specific heat. As the temperature is lowered, Cu^{2+} ions coupled by the strongest J_2 will form a singlet state at first. The formation of the singlet J_2-dimer state corresponds to the higher temperature peak observed at around 19 K, whose value is comparable with $J_2 = 24$ K. As the temperature is further lowered, magnetic correlation among spins on monomer Cu^{2+} ions in between J_2 dimers will develop with effective interaction J_{eff} mediated by the J_2

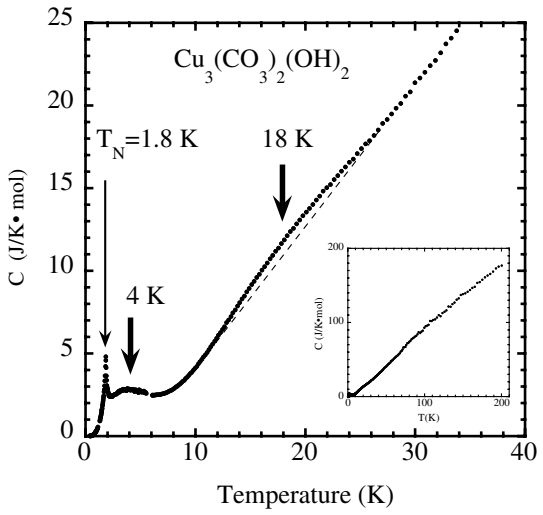

FIG. 4. The temperature dependence of the low temperature specific heat. Inset is the specific heat for the entire temperature range. A broken line is a guide for the eyes to make an anomaly at around 18 K clearer. Note that a lattice contribution is not subtracted.

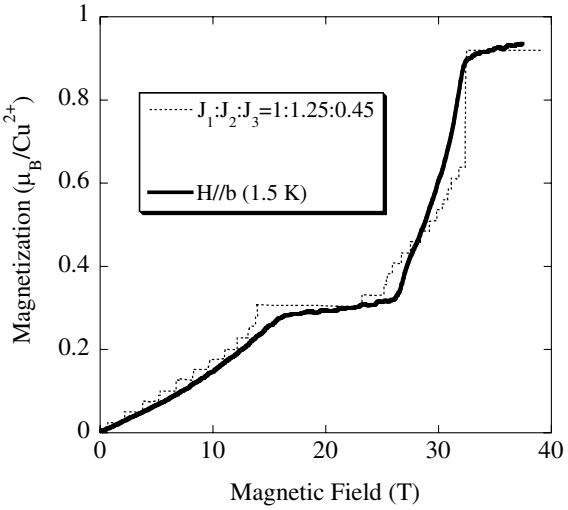

FIG. 5. The best fitting result for the magnetization curve at 1.5 K for $H \parallel b$ with the theoretical dotted line using J_1:J_2:J_3 = 1:1.25:0.45.

dimer. The lower temperature peaks found at 5 K for $\chi(T)$ and 4 K for $C(T)$ would be associated with a 1D short-range spin ordering developed below a temperature corresponding to $J_{\rm eff}$. Bonner and Fisher studied the 1D Heisenberg antiferromagnet with the nearest-neighbor interaction J to find relations: $k_B T_{\rm max}[C]/J = 0.481$ and $k_B T_{\rm max}[\chi]/J = 0.641$ [17], where k_B is Boltzmann constant. Using these relations, $J_{\rm eff}$ is estimated to be 8.3 K from $T_{\rm max}[C] = 4$ K or 7.8 K from $T_{\rm max}[\chi] = 5$ K. The theoretical expression for $J_{\rm eff}$ is given in Ref [16] obtained by a perturbation calculation up to the 5th order of J_1/J_2. Putting the determined parameters J_1, J_2, and J_3 into the expression for $J_{\rm eff}$, we obtain $J_{\rm eff} = 13.8$ K, which apparently agrees with the experimental results. However, the 5th order perturbation is found to be comparable to the 2nd order one so that the calculation does not tend to converge in our case of $J_1/J_2 = 19/24$. The calculated value is hence not reliable. A theory beyond the perturbation is desired.

Finally, we are going to discuss the magnetic anisotropy observed in the magnetization results. The 1/3 plateaux are observed in the magnetic field range from 16 to 26 T for $H \parallel b$ and 11 to 30 T for $H \perp b$, so that the plateau range is 90% wider for $H \perp b$ than $H \parallel b$. The most plausible origin of the magnetic anisotropy is the Dzyaloshinskii-Moriya (DM) interaction since there is no point symmetry in the azurite and the single-ion anisotropy does not exist in Cu^{2+} ($S = 1/2$) magnetic systems. We calculated the magnetization curve taking into account the DM interaction using the exact diagonalizaton method on a finite spin chain. We assumed that the D vector of the DM interaction is perpendicular to both the J_2-dimer bond and to the b axis, on a basis of approximate crystallographic mirror planes. We calculate the magnetization for several ratios of the DM vector D to J_2. We have found that the 1/3 plateau region for $H \perp b$ (or, $H \parallel D$) is enlarged by 57% (89%) if D/J_2 is set to 0.2 (0.3), compared to the plateau region without the DM interaction. On the other hand, it does not change even if D/J_2 was increased up to 0.3 for $H \parallel b$. Our experimental result is hence qualitatively explained provided that the DM interaction of $D/J_2 = 0.3$ is present in azurite. As shown in Fig. 2, the magnetization does not reach the expected value of the saturation magnetization at H_{c3} and increased gradually above H_{c3}. Furthermore, the magnetization is not exactly constant in the plateau region but increases slowly as the magnetic field is increased. These features are also reproduced in the calculated magnetization with the DM interaction for $H \parallel b$ (i.e., $H \perp D$) due to off-diagonal elements of the DM interaction. We considered only DM interaction on J_2 bond in the above calculation. It is possible DM interaction is present on other magnetic bonds, such as J_1 or J_3. More detailed comparison of the experiments to the calculations will be reported in a future paper.

In summary, we have measured the magnetic susceptibility, the high field magnetization and the specific heat of a $Cu_3(CO_3)_2(OH)_2$ single crystal , the model material of the distorted diamond chain. The magnetization curve has a definite plateau at one third of the saturation magnetization. The exchange interactions are determined to be $J_1 = 19$ K, $J_2 = 24$ K, $J_3 = 8.6$ K by comparing experimental results with theoretical calculations. Two broad peaks, observed at around 20 and 5 K both in the magnetic susceptibility and the specific heat measurements, suggest that the magnetic short-range order develops in a two-stage process. The magnetic anisotropy observed in the magnetization can be explained if the DM interaction of $D/J_2 = 0.3$ is present.

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