Magnetic phase diagram of the frustrated \( S=1/2 \) triangular-lattice magnet \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \)

H. Kikuchi\(^1\), N. Kasamatsu\(^1\), Y. Ishikawa\(^1\), Y. Koizumi\(^1\), Y. Fujii\(^2\), A. Matsuo\(^3\), K. Kindo\(^3\)

\(^1\)Department of Applied Physics, University of Fukui, Fukui 910-8507, Japan
\(^2\)Research Center for Development of Far-Infrared Region, University of Fukui, Fukui 910-8507, Japan
\(^3\)Institute for Solid State Physics, The University of Tokyo, 277-8581 Kashiwa, Japan
E-mail: kikuchi@u-fukui.ac.jp

Abstract. \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) (rouaite) is a frustrated triangular lattice magnet. We measured the magnetic susceptibility, specific heat, \(^1\)H-NMR and high field magnetization of a powder sample of \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) and found a clear evidence of the long range magnetic order at about 8 K. The transition temperature was found to decrease as the magnetic field \( H \) increased. An \( H-T \) phase diagram of \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) was determined by specific heat, magnetization and \(^1\)H-NMR data. The high field magnetization curve was analyzed using a simple spin model.

1. Introduction

Geometrically frustrated magnets have attracted much interest recently, because some new physical states including spin liquids are expected to be realized in them [1]. Triangular lattice antiferromagnet is a representative example of the frustrated system and has been extensively studied [1]. \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) (mineral name rouaite) is one of the triangular lattice antiferromagnets. The crystal structure of \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) is monoclinic (space group: \( \text{P2}_1 \)) and contains two crystallographically different sites of \( \text{Cu}^{2+} \) ions [2]. Site one (Cu1) is surrounded by four OH groups and two NO\(_3\) groups, and site two (Cu2) is surrounded by five OH groups and one NO\(_3\) group.

The \( \text{Cu}^{2+} \) ions are coupled via oxygen ions to form a distorted triangular lattice as shown in Fig. 1. Six different intralayer exchange couplings \( J_i (i = 1 \sim 6) \) between \( \text{Cu}^{2+} \) ions can be present. The values of these exchange couplings, which depend on the bond length and bond angle, have been calculated using the Hückel model [3], density functional theory (DFT) and the quantum Monte Carlo method [4]. Detailed calculations of the electron density distribution of \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) have also been reported [5]. The values obtained using the quantum Monte Carlo method were calculated as \( J_1(\text{F})=14, J_2(\text{AF})=-34.9, J_3(\text{F})=6.9, J_4(\text{F})=10.4, J_5(\text{AF})=-4.9 \) and \( J_6(\text{F}) = 2.0 \text{ cm}^{-1} \) [4], where F and AF denotes ferromagnetic and antiferromagnetic interaction, respectively. These values suggest that the spin system in \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) is composed of a dominant ferromagnetic \((J_1)\) chain and an antiferromagnetic \((J_2)\) chain. Both F and AF chains are coupled by other smaller frustrating exchange interactions \((J_3 \sim J_6)\). Because the spin system of \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) contains both properties of a one-dimensional quantum chain and a frustrated magnet, the spin system of this compound is very unique. The magnetic
Figure 1. Crystal structure of Cu$_2$(NO$_3$)(OH)$_3$. Larger spheres represent Cu (red), and smaller ones represent O (light blue). $J_i$ ($i=1$-$6$) (black line) represent different exchange constants between copper ions.

susceptibility $\chi(T)$ of Cu$_2$(NO$_3$)(OH)$_3$ was measured using either a powder sample [6] or a single crystal [3]. $\chi(T)$ of the powder sample has been reported to have a round maximum at 12 K, which has been discussed with respect to an occurrence of a long range order (LRO) although the possibility of a short range order (SRO) was not excluded because a neutron diffraction experiment on a deuterated sample did not detect the magnetic order [6]. $\chi(T)$ of the single crystal had a maximum at around 8 K and was analyzed using the antiferromagnetic chain model without a LRO. There is some controversy whether or not there is a magnetic LRO in Cu$_2$(NO$_3$)(OH)$_3$. The most convincing evidence of a thermodynamic phase transition is given by specific heat data. In this paper, we report measurements results of the specific heat of Cu$_2$(NO$_3$)(OH)$_3$ and present a clear evidence of the LRO. In addition, we measure magnetic susceptibility, high field magnetization and $^1$H-NMR to give the field-temperature ($H$-$T$) phase diagram of Cu$_2$(NO$_3$)(OH)$_3$.

2. Experiments
Powder samples of Cu$_2$(NO$_3$)(OH)$_3$ were synthesized by a hydrothermal method, according to the procedure reported in Ref. [7]. The quality of the specimen was investigated by powder X-ray diffraction. All the measurements were performed using the prepared powder sample. Magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design) in the temperature range of 2-300 K. High-field magnetizations of up to about 60 T were measured using a pulsed high magnet at the Institute for Solid State Physics. Specific heat measurements were performed using a Quantum Design PPMS by the relaxation method under an applied field of up to 13 T. $^1$H-NMR spectra were measured by recording the spin-echo intensity while sweeping the magnetic field. Nuclear spin-lattice relaxation time $T_1$ was measured by the inversion recovery method.

3. Results and Discussion
Figure 2 shows the molar magnetic susceptibility $\chi(T) = M/H$, where $M$ and $H$ is magnetization and magnetic field, respectively, and the corresponding reciprocal susceptibility measured in a magnetic field of $H = 0.01$ T for temperatures between 2 and 300 K. The higher temperature part of $\chi(T)$ follows the Curie-Weiss law. The Weiss temperature $\Theta$ was estimated to be about 6 K, which is slightly different from the reported value of - 8 K [3]. The Curie constant $C$ was evaluated to be 0.72 emu-K/mol. The effective magnetic moment of the Cu$^{2+}$ ion was estimated to be 1.70 $\mu_B$, which is comparable to the expected value of 1.73 $\mu_B$ for a Cu$^{2+}$ ion with $g = 2$. A broad peak is observed at around $T_{\text{max}} = 11$ K. This behavior agrees well with the reported result [6]. An inset of Fig. 2 shows the field dependence of $\chi(T)$ at low temperatures. As the magnetic field increases, the broad peak shifts toward a lower temperature.
Figure 2. Temperature dependence of the magnetic susceptibility $\chi(T) = M/H$ and the corresponding reciprocal susceptibility measured at a magnetic field of $H = 0.01 T$. Inset shows the low temperature part of $\chi(T)$ measured at various magnetic fields up to 7 T. Solid line is the Curie-Weiss fitting with Weiss temperature $\Theta = 6 K$ and Curie constant $C = 0.72 \text{ emu·K/mol}$.

Figure 3. Specific heat data of Cu$_2$(NO$_3$)(OH)$_3$ measured under an applied magnetic field of up to 13 T.

Figure 3 shows the heat capacity measured at magnetic fields up to 13 T. Lattice contributions are not subtracted from the data because no isostructural material of Cu$_2$(NO$_3$)(OH)$_3$ without magnetic ions is known. A distinct $\lambda$-type anomaly was observed at $T_N = 8 K$ in the zero field data. This finding is a clear evidence of the occurrence of magnetic LRO in this magnet.

Figure 4 shows the high field magnetization of Cu$_2$(NO$_3$)(OH)$_3$ measured at 4.2 and 1.3 K. The field derivative of the magnetization, $dM/dH$, is also shown. The saturation magnetization $M_s$ per chemical formula unit is given by $M_s = nSg\mu_B \approx 2\mu_B$ where $n = 2$ is the number of magnetic Cu$^{2+}$ ions in a formula unit, $g$ is Lande’s $g$-factor, $\mu_B$ is the Bohr magneton and $S$ is the spin number, $1/2$. $dM/dH$ shows very sharp peaks at around 2 T, and 14 T (1.3 K) or 11 T (4.2 K), which indicate the occurrence of field-induced magnetic transitions. The lower field transition at around 2 T is also observed in our magnetization measurement using the MPMS magnetometer and could be assigned to a spin-flip transition. The higher
Figure 4. High field magnetization curve measured at 1.3 K (blue line) and 4.2 K (red line). The field derivative of the magnetization at 4.2 K is shown in the arbitral unit. The solid curve is the model calculation at $T=0$ in which the spin system is assumed to be composed of mutually independent F- and AF- chains. The dotted line demonstrates the contribution from the fully polarized F-chain at $T=0$ to the magnetization. The contribution from AF-chain is calculated with $J_2 = -34.9 \text{ cm}^{-1}$ and $g=2.23$.

The field transition corresponds to the LRO transition observed in the specific heat measurement. Besides these field-induced transitions, the magnetization curve has a unique property. It is easily seen that an increase rate of the magnetization becomes smaller above around 20 T where the magnetization reaches about one half of the saturation magnetization $M_s$. Because this field range is above the phase transition field, the magnet is in a paramagnetic phase, not in the classical magnetic ordered phase. We tried to explain this result using a simple model in which only the dominant $J_1$ and $J_2$ interactions are considered and other smaller interactions are neglected. In this simple model, the spin system is composed of the independent ferromagnetic and antiferromagnetic chains. The ferromagnetic chain is assumed to be fully polarized in this higher field range at low temperature and contributes to one half of the saturation magnetization. The magnetization curve originated from the antiferromagnetic chain is calculated using the theoretical result obtained by the density matrix renormalization group method [8] with $J_2 = -34.9 \text{ cm}^{-1}$ and $g=2.23$ [4]. A saturation field $H_s$ is given by $H_s = 2|J_2|k_B/g\mu_B = 68 \text{ T}$, where $k_B$ is the Boltzmann constant. The calculated curve based on the model is plotted in Fig. 4 as the solid line. Considering that our approximate model is very rough, the calculation qualitatively agrees with the observed curve in the higher field region. A point of note is that the magnetization above approximately 20 T follows the characteristic downward convex curve of the 1D Heisenberg antiferromagnet. Remembering that such a feature represents the quantum nature of the 1D magnet, the quantum nature of the system is recovered in a state where the classical magnetic ordered phase is collapsed.

In order to study the magnetic order of Cu$_2$(NO$_3$)(OH)$_3$ from microscopic point view, we measured $^1$H-NMR spectra and $T_1$. Observed relaxation data against time $t$ are analyzed using the stretched exponential function, $\exp(-t/T_1^\beta)$ where $\beta$ is a stretch exponent. Figure 5 shows the temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ of $^1$H-NMR measured at operating radio frequencies of 42.3, 213 and 298 MHz. A very sharp peak is observed at around 7 K, reflecting the occurrence of the magnetic order. In the ordered phase below 7 K, $T_1^{-1}$ is found to follow the $T^3$ law, which is expected to be satisfied for the magnon relaxation process in the ordered antiferromagnet [9]. Value of $\beta$ is about one in the paramagnetic phase, and 0.6~0.7
in the ordered phase well below 7 K. Just at around $T_N$, $\beta$ takes small value down to about 0.2, suggesting that the relaxation times for protons in the sample are strongly inhomogeneous at $T \approx T_N$ depending probably on the crystal orientation against the applied field.

Figure 6 shows $^1$H-NMR spectra measured at 42.3 MHz. As the temperature decreases, sharp peaks of $^1$H observed in the paramagnetic phase turn into very broadened pattern below $T_N$. The pattern at 1.5 K has characteristic rectangular pattern, which is expected for a powder sample with an antiferromagnetic ordered phase [10]. These NMR data indicate that the ordered phase of \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) has a typical antiferromagnetic nature. We need further study to determine precise spin structure using a single crystal.

All collected data concerning the magnetic transition of \( \text{Cu}_2(\text{NO}_3)(\text{OH})_3 \) is summarized in the
Figure 7. Field-temperature (H-T) phase diagram of Cu$_2$(NO$_3$)(OH)$_3$. Points are determined from heat capacity, magnetization and NMR measurements. SF and AF stand for spin-flip and antiferromagnetic phase, respectively.

H-T phase diagram (Fig. 7). The field dependence of $T_{\text{max}}$ is also plotted in the phase diagram. The magnetic order temperature $T_N$ monotonically lowers as the magnetic field increases. Note should be paid that $T_N$ is lower than $T_{\text{max}}$. This result suggests that there is a crossover region in the phase diagram (the region described as 'SRO' in Fig. 7) where the LRO does not occur, probably due to the spin frustration, although the short range spin correlation is well developed. The same behavior has been observed in the frustrated triple-chain magnet Cu$_3$(OH)$_4$SO$_4$ (antlerite) [11], which has several exchange interactions. This behavior may be a universal feature of a frustrated system containing multiple magnetic interactions.

To conclude, we measured the magnetic susceptibility, specific heat, $^1$H-NMR spectra and high field magnetization of a powder sample of Cu$_2$(NO$_3$)(OH)$_3$ and found clear evidence of the long range magnetic order at about 8 K. The H-T phase diagram of Cu$_2$(NO$_3$)(OH)$_3$ was determined by specific heat, magnetization and NMR data. The high field magnetization curve was analyzed using a simple spin model.

This research was supported by JSPS KAKENHI Grant Number 17K05515.

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