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Novel three-dimensional magnetic ordering in the quantum spin system NH_4CuCl_3

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Abstract. Low-temperature specific heat and magnetization measurements have been performed on the quantum spin system NH_4CuCl_3 which has magnetization plateaus at one-quarter and three-quarters of the saturation magnetization. It is found that the present system undergoes three-dimensional magnetic ordering at $T_N = 1.3$ K. It is suggested that one-quarter of the spins are ordered below T_N, and the remaining spins are in the singlet state. The small magnetic entropy at T_N indicates that the phase transition occurs under the condition of a well-developed spin correlation around T_N. The field dependence of the three-dimensional ordering is also investigated on the basis of magnetization measurements. Based on this evidence, a magnetic phase diagram for NH_4CuCl_3 is proposed.

1. Introduction

In the last few years, the phenomenon of magnetization plateaus in one-dimensional spin systems has provoked intense speculation. It is predicted that magnetization will exist at one-third of the saturation magnetization M_s in a spin-$\frac{1}{2}$ Heisenberg chain with ferromagnetic–ferromagnetic–antiferromagnetic interactions [1, 2] and an antiferromagnetic three-leg ladder [3], and at half of M_s in a spin-$\frac{1}{2}$ antiferromagnetic alternating Heisenberg chain with next-nearest-neighbour interactions [4, 5] and a spin-1 antiferromagnetic alternating Heisenberg chain [6,7]. A recent theory, developed by Oshikawa *et al* [8], suggested that the magnetization plateau can exist only when the condition $n(S - m) =$ an integer is satisfied, where n is the period of the ground spin state, S is the magnitude of the spin, and m is the magnetization per site in units of $g\mu_B$.

Experimentally, the magnetization plateau has been observed at half of M_s in a spin-1 antiferromagnetic alternating chain system $[Ni_2(\text{methyl-bis(3-aminopropyl)amine})_2(\mu\text{-ox})(\mu\text{-}N_3)]ClO_4{\cdot}0.5H_2O$ [9], which satisfies the theoretical prediction [6, 7]. Magnetization plateaus have also been reported for a two-dimensionally coupled antiferromagnetic dimer system, $SrCu_2(BO_3)_2$ [10].

In our previous paper [11], we reported that the magnetization curve of NH_4CuCl_3 has plateaus at one-quarter and three-quarters of the saturation magnetization M_s. This compound is isostructural with $KCuCl_3$, which belongs to the monoclinic space group $P2_1/c$ [12, 13]. The crystal structure is composed of double chains of edge-sharing $CuCl_6$ octahedra along the *a*-axis. The double chains are located at the corners and centre of the unit cell in the *bc*-plane, and are separated by NH^{4+} ions. In the double chain, there are three kinds of nearest-neighbour

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interaction, J_1, J_2, and J_3, which may be described as a spin-$\frac{1}{2}$ alternating Heisenberg chain consisting of J_2- and J_3-interactions with next-nearest-neighbour interactions J_1 [14, 15].

The origin of the magnetization plateaus observed in NH_4CuCl_3 is not attributed to the magnetic anisotropy, but to the quantum effect, because the plateaus appear in every external field direction. We did not observe magnetization plateaus at $M = 0$ and $\frac{1}{2}M_s$, as was expected from theoretical calculation for the spin-$\frac{1}{2}$ antiferromagnetic alternating Heisenberg chain with next-nearest-neighbour interactions [4,5]. Since the slope of the magnetization curve near zero field is finite even at $T = 0.5$ K, it is suggested that NH_4CuCl_3 has a gapless magnetic ground state. It is evident that the ground state of NH_4CuCl_3 is different from those of isostructural $KCuCl_3$ and $TlCuCl_3$; each of these has a singlet ground state with an excitation gap [14–18]. It is considered from susceptibility data [11] that the intrachain dominant interactions J_2 in NH_4CuCl_3 are much weaker than those in $KCuCl_3$ and $TlCuCl_3$. Neutron inelastic scattering data for $KCuCl_3$ [17,18] strongly suggest that the interactions between the double chains cannot be neglected, and that they are of the same order of magnitude as the J_1- or J_3-interactions in the double chain. Thus, the gapless ground state at zero field in NH_4CuCl_3 is understood to arise from the interchain interactions.

Some theoretical and experimental studies on quasi-one-dimensional antiferromagnetic systems reveal that three-dimensional (3D) magnetic ordering can occur due to finite interchain coupling [19, 20]. For example, in $(CH_3)_4NMnCl_3$ (TMMC), 3D magnetic ordering occurs at $T_N = 0.84$ K with the help of the weak interchain interaction ($J'/J \sim 1 \times 10^{-4}$), and the transition temperature T_N shows field dependence [20].

In spin-gap systems, the external magnetic field suppresses the gap. When the applied field is higher than the critical field corresponding to the gap, the ground state becomes gapless, so 3D magnetic ordering can occur. Such a field-induced phase transition has been reported for a spin-$\frac{1}{2}$ Heisenberg ladder system Cu_2(1, 4-diazacycloheptane)$_2Cl_4$ [21, 22], Haldane systems $Ni(C_5H_{14}N_2)_2N_3(ClO_4)$ [23] and $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ [24], and spin-$\frac{1}{2}$ alternating chain systems $Cu(NO_3)_2{\cdot}2.5H_2O$ [25] and $(CH_3)_2CHNH_3CuCl_3$ [26]. Field-induced 3D magnetic ordering was also observed in $TlCuCl_3$ [27] which is isomorphous with NH_4CuCl_3.

In NH_4CuCl_3, no anomaly indicative of the phase transition was seen in the susceptibility data down to 1.7 K, as reported previously [11]. In order to investigate the magnetic phase transition in NH_4CuCl_3, which is expected from the gapless ground state, we carried out specific heat and magnetization measurements down to 0.4 K. We report the results in this paper.

2. Experimental procedures

Single crystals of NH_4CuCl_3 were grown by the method described in reference [11]. Crystals of nonmagnetic NH_4CdCl_3 were also prepared to evaluate the nonmagnetic part of the specific heat. NH_4CdCl_3 crystallizes in an orthorhombic structure (space group $Pnam$) [28], which is a prototype of that of NH_4CuCl_3. The distortion of this structure is due to the Jahn–Teller effect. The single crystals of NH_4CdCl_3 were obtained by the slow evaporation of an aqueous solution containing equimolar quantities of NH_4Cl and $CdCl_2$ at room temperature.

Specific heat measurements at zero magnetic field have been performed by an adiabatic heat-pulse method between 0.4 and 20 K. The specific heat of NH_4CdCl_3 was also measured to estimate the lattice part of the specific heat of NH_4CuCl_3. Magnetization measurements have been performed using an extraction-type magnetometer. The magnetic fields were applied parallel to the a-axis. The magnetization data were collected between 0.6 and 4.5 K at magnetic fields of 0.5, 1.0, and 6.0 T. These measurements were performed at the Ishikawa Laboratory

and at the Ultrahigh Magnetic Field Laboratory, Institute for Solid State Physics, the University of Tokyo.

3. Results and discussion

3.1. Specific heat

Figure 1 shows the specific heat of NH_4CuCl_3 and NH_4CdCl_3 between 0.4 and 15 K. It is considered that the specific heat of NH_4CdCl_3 represents the nonmagnetic part of the specific heat of NH_4CuCl_3, because its crystal structure is a prototype of that of NH_4CuCl_3 [28]. We evaluate the magnetic specific heat by subtracting the specific heat of NH_4CdCl_3 from that of NH_4CuCl_3. Figure 2 shows the magnetic specific heat C_m of NH_4CuCl_3 with an error deviation about 0.05 J K^{-1} mol^{-1} for $T < 4$ K and about 0.30 J K^{-1} mol^{-1} for $T > 4$ K while the inset shows C_m for $T < 4.2$ K. The magnetic entropy S_m is obtained by integrating C_m/T with respect to T as shown in figure 3. Since the spin value of the present system is $S = 1/2$, the full entropy is given by $R \ln 2 = 5.76$ J K^{-1} mol^{-1}.

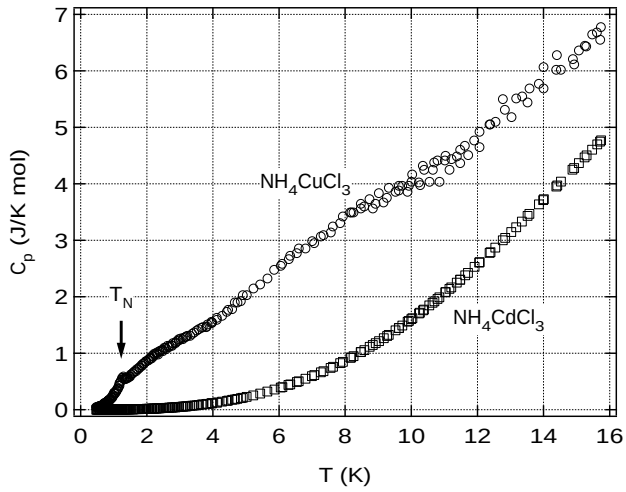

Figure 1. The specific heat of NH_4CuCl_3 and NH_4CdCl_3. The arrow indicates the phase transition at 1.3 K.

A sharp anomaly in the specific heat is observed at $T_N = 1.3$ K. This anomaly is considered to be due to 3D (long-range) magnetic ordering as expected from the gapless ground state. The value of the magnetic entropy at T_N is approximately $0.03R \ln 2$. The small entropy at T_N indicates that a magnetic phase transition occurs under the condition of well-developed spin correlation.

The magnetic specific heat has a broad maximum at around 9 K. The broad maximum is understood to indicate the development of the spin correlation, which may correspond to the broad shoulder in the susceptibility observed at around 15 K [11]. It is also noted that the magnetic specific heat has a broad shoulder between T_N and 4 K. Since the magnetization curve exhibits the first plateau at $\frac{1}{4}M_s$, it is deduced that three-quarters of the spins are in the singlet state with the excitation gap at zero field, and the remaining spins are coupled to each other to produce the gapless state. The three-quarters of the spins are able to produce the Schottky-type specific heat.

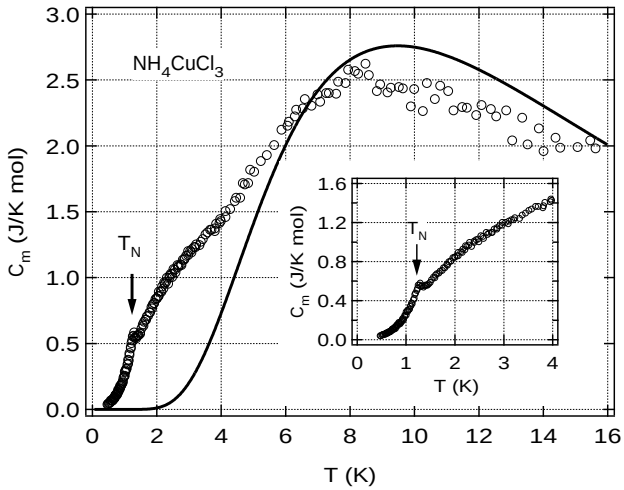

Figure 2. The magnetic specific heat of NH_4CuCl_3. The solid line is a calculation result for the Schottky-type specific heat. The inset shows the low-temperature specific heat.

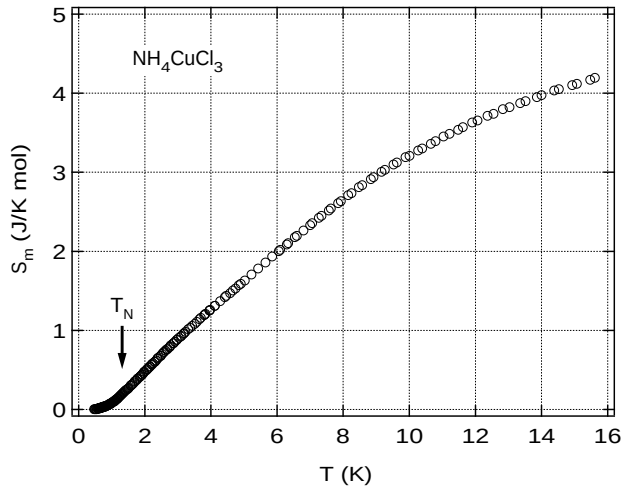

Figure 3. The magnetic entropy of NH_4CuCl_3.

We roughly estimate the Schottky-type specific heat, assuming that all of the spin pairs in the singlet state are isolated from each other, and that two-thirds of the pairs have a gap $\Delta_1 = g\mu_B(H_{c2} + H_{c3})/2$ and the remainder of them have a gap $\Delta_2 = g\mu_B(H_{c4} + H_s)/2$, where H_{c2}, H_{c3}, H_{c4}, and H_s are the edge fields of magnetization plateaus. Then the Schottky-type specific heat is described by

$$C_{\mathrm{Sch}} = \sum_{i=1,2} \frac{N_i \Delta_i^2}{k_B T^2} \frac{3\exp(\Delta_i/k_B T)}{[3 + \exp(\Delta_i/k_B T)]^2} \tag{1}$$

where $N_1 = N/4$ and $N_2 = N/8$ with the number of spins N. The solid line in figure 2 is the Schottky-type specific heat calculated with $g_a = 2.17$, $\Delta_1 = 3.08 \times 10^{-22}$ J, and

$\Delta_2 = 5.42 \times 10^{-22}$ J. The broad maximum at around 9 K is roughly described by equation (1).

Thus, we suggest that the broad maximum at around 9 K is mainly attributable to the Schottky-type specific heat produced by the three-quarters of the spins, and that the broad shoulder between T_N and 4 K is due to the development of the short-range order for the remaining spins, which are responsible for the gapless ground state. The latter suggestion is compatible with the entropy of $S_m \approx \frac{1}{4}R \ln 2 = 1.44$ J K^{-1} mol^{-1} at 4 K.

3.2. Low-temperature magnetization

In a previous study [11], we reported the susceptibility of NH_4CuCl_3 data down to 1.7 K. The susceptibility data demonstrate a broad maximum at around 4 K, and then a decrease with decreasing temperature. It is noted that the broad maximum has a broad shoulder at around 15 K as previously mentioned. However, the susceptibility below 1.7 K is not known.

Figure 4 shows the low-temperature magnetization measured at $H = 0.5$, 1.0, and 6.0 T for $\boldsymbol{H} \parallel \boldsymbol{a}$. For $H = 0.5$ and 1.0 T, the anomaly due to the phase transition is seen at $T_N \approx 1.3$ K, which is in agreement with the specific heat result. The magnetization is nearly constant up to the transition temperature T_N. As the temperature is increased from T_N, the magnetization increases rapidly and produces a broad maximum at around 4 K in agreement with our previous data [11]. A small shift in transition temperature is observed on increasing the external magnetic field up to 1 T. Thus, it is suggested that when the external field is low, the transition temperature will increase as the field is increased.

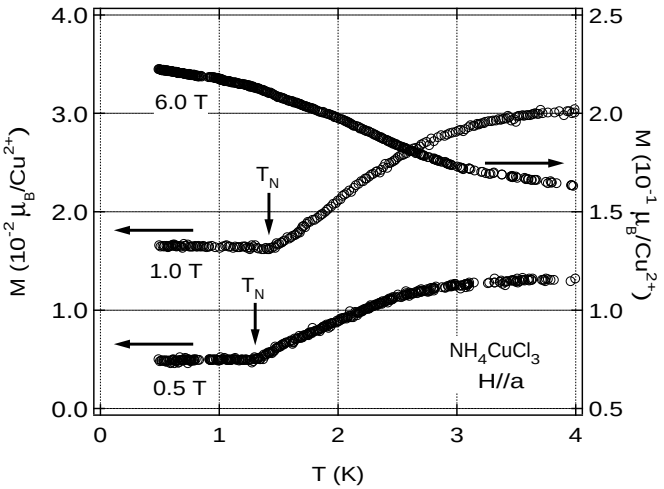

Figure 4. The low-temperature magnetization measured at $H = 0.5$, 1.0, and 6.0 T for $\boldsymbol{H} \parallel \boldsymbol{a}$. The arrows indicate the transition temperature.

It is noted that no phase transition is observed at $H = 6.0$ T. With decreasing temperature, the magnetization for $H = 6.0$ T increases monotonically, and has no broad maximum around 4 K. For $\boldsymbol{H} \parallel \boldsymbol{a}$, the first magnetization plateau appears between $H_{c1} = 5.0$ T and $H_{c2} = 12.8$ T. Our previous ESR measurements [29] revealed that in the plateau region there exists a finite gap between the ground state and the lowest excited state. Thus, the ground state is gapped at $H = 6.0$ T. When the ground state is gapped, a magnetic phase transition does not occur. The absence of a phase transition at $H = 6.0$ T is consistent with the gapped ground state.

Although we have not measured the magnetizations for $1 < H < 6$ T, we may deduce that a phase transition can occur for $H < H_{c1}$ where the ground state is gapless.

3.3. Phase diagram

It was found by the present specific heat and magnetization measurements that a magnetic phase transition occurs at $T_N = 1.3$ K at zero field, and that the transition temperature depends on the external field. The present system does not undergo a phase transition at $H = 6.0$ T where the ground state is gapped.

From the high-field magnetization measurement at 0.5 K, field-induced phase transitions were detected at $H_{c1} = 5.0$ T, $H_{c2} = 12.8$ T, $H_{c3} = 17.9$ T, $H_{c4} = 24.7$ T, and $H_s = 29.1$ T for $\boldsymbol{H} \parallel \boldsymbol{a}$ [11]. Plateaus appear between H_{c1} and H_{c2}, and H_{c3} and H_{c4}. The ground state in the plateau regions is gapped. The gap is described as $\Delta = g\mu_B(H - H_{lc})$ for $H_{lc} < H < (H_{lc} + H_{hc})/2$ and $\Delta = g\mu_B(H_{hc} - H)$ for $(H_{lc} + H_{hc})/2 < H < H_{hc}$, where H_{lc} and H_{hc} are the lower and higher edge fields of the plateau, respectively [29]. The ground state is gapless for $H < H_{c1}$, $H_{c2} < H < H_{c3}$, and $H_{c4} < H < H_s$. Therefore, a phase transition can occur in these field ranges. We propose a phase diagram for the magnetic field versus the transition temperature as shown in figure 5, where the magnetic field is normalized by the g-factor. Since the magnetic anisotropy is negligible in NH_4CuCl_3 [11, 29], the phase diagram may be independent of the field direction when normalized by the g-factor. The present experimental and previous high-field magnetization process results are plotted as closed and open circles, respectively. The solid lines are a guide to the eye and represent the prediction of the phase boundaries. In the magnetization curve at 4.2 K, an anomaly is seen for the transition between the paramagnetic phase and phase II, while no anomaly is seen for the transition between the paramagnetic phase and phase I and between the paramagnetic phase and phase III. Thus, the highest transition temperature in phase II should be higher than those in phases I and III.

Because the values of the magnetization at the first and second plateaus are $\frac{1}{4}M_s$ and $\frac{3}{4}M_s$, respectively, the following is suggested. In phase I, one-quarter of the spins are ordered, and the

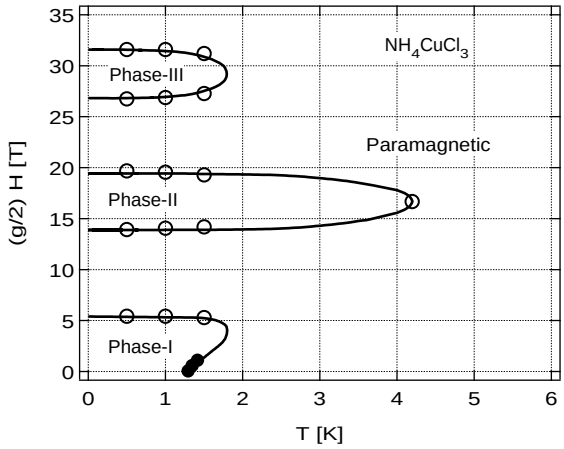

Figure 5. The proposed magnetic phase diagram for NH_4CuCl_3. The solid lines are guides to the eye. The closed and open circles indicate the present experimental and previous high-field magnetization process [11] results, respectively.

remaining spins are in the singlet state. In phase II, three-quarters of the spins are ordered, and all spins are ordered in phase III. For the spin state at zero temperature in NH_4CuCl_3, several models have been proposed theoretically [30, 31]. At present, however, the spin structure in each phase is not known. Studies of the elastic neutron scattering and NMR measurements are necessary to determine the spin structure.

4. Conclusions

The three-dimensional magnetic ordering in the quantum spin system NH_4CuCl_3 has been studied by conducting specific heat and magnetization measurements down to 0.4 K. Magnetic ordering is detected at $T_N = 1.3$ K at zero field. The small magnetic entropy $S_m \approx 0.03R \ln 2$ at T_N indicates that the phase transition occurs under the condition of well-developed spin correlation. It is suggested that one-quarter of the spins are ordered below T_N, and the remaining spins are in the singlet state. In a lower magnetic field, the transition temperature increases with increasing field. However, no phase transition is observed at $H = 6.0$ T. This finding indicates that the transition temperature strongly depends on the external field. Based on this evidence and the results of our previous high-field magnetization measurements, a magnetic phase diagram for NH_4CuCl_3 is proposed, as shown in figure 5.

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