Low-Temperature Magnetization Study of Spin Gap System \((\text{CH}_3)_2\text{NH}_2\text{CuCl}_3\) with Nanometer Particle Size

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Abstract. So far specific heat measurements for the title compound have revealed that the magnetic field vs. temperature phase diagram depended significantly on the system size. For instance, the single crystal showed the spontaneous magnetic ordered phase in low fields and the field induced one in high fields separated by the magnetization plateau range at around 3 T. While the powder sample with typically nanometer particle size showed a quite different trend that field induced magnetic ordered phase extended to zero field. In this study, we measured dc magnetization of powder sample and nano-sized powder sample. Measurements were performed down to the lowest temperature of 0.5 K using commercial Quantum Design MPMS equipped with homemade \(^3\)He refrigerator insert. Most remarkable feature is that 1/2 plateau was not observed clearly in the magnetization process for the nano-sized powder sample indicating the disappearance of the spin gap.

1. Introduction

The title compound DMACuCl\(_3\) (DMA = \((\text{CH}_3)_2\text{NH}_2\)) is considered to be one of the spin-gapped systems that have recently attracted considerable attention. Among others the magnetic properties of DMACuCl\(_3\) clarified so far are quite peculiar. Such peculiarity is based on the presence of ferromagnetically coupled dimer (F-dimer) and antiferromagnetically coupled dimer (AF-dimer) connected alternatively by the weak inter-dimer interaction along the structural one dimensional chain [1][2]. As a result, this system shows quite unique field versus temperature \((H-T)\) phase diagram as shown in Figure 1 [3][4]. In this figure, results of our previous specific heat studies for single crystal (open triangles), powder sample (open circles) and nano-sized powder sample (open squares) are presented.

In the single crystal, there are two kinds of magnetic ordered phases. One is a spontaneous magnetic ordered (SMO) phase in low fields and the other is the field induced magnetic ordered (FIMO) one in high fields separated by the narrow field range at around 3 T, where 1/2 magnetization plateau takes place. This result is considered to be reflecting the distinct energy levels of F-dimer and AF-dimer separated by the finite spin gap. In other words, F-dimers and AF-dimers are responsible for the appearance of SMO and FIMO phases, respectively. Although
the magnetic network between structural chains is not fixed precisely at the moment, such a qualitative scenario mentioned above may be applicable to the result for the single crystal [5][6].

However, the powder sample shows slightly different phase diagram as represented in the vicinity of FIMO phase. The apex of critical temperature $T_c$ for FIMO phase is about 7 T in the single crystal, and it decreases toward 0 K with decreasing the magnetic field as usually expected. By contrast, the powder sample shows opposite behaviors that $T_c$ increases slightly with decreasing the field [7]. Such unexpected behaviors are enhanced in the nano-size powder sample. The FIMO phase is extended to lower field and seems to be realized even at zero magnetic field (We call this phase as Extended FIMO). This may be due to the effect of end spins appeared on the surface of crystal. It is naturally expected that smaller the particle size, stronger the effect of end spins to the host system. The presence of end spin is not evidenced directly so far, but at least it is consistent with the experimental facts that the deviation of phase boundary from the single crystal is more significant in the nano-sized sample than in the powder sample.

Interestingly, the SMO phase still exists in the resultant phase diagram for the nano-sized sample and seems to be not so affected by the FIMO phase appeared in the high temperature range. This may indicate that the coexistence of SMO and FIMO phases is realized in the nano-sized DMA$\text{CuCl}_3$. In a separated paper, such possibility is discussed in detail based on the results of specific heat and ESR measurements [8].

Here, we report the result of magnetization measurements at low temperatures down to 0.5 K for powder and nano-sized powder samples of DMA$\text{CuCl}_3$. The presence and an effect of end spin is examined through the comparison between both samples.

2. Experimental
The single crystal of DMA$\text{CuCl}_3$ was easily obtained by slow evaporation of 1:1 solution of CuCl$_2$-2H$_2$O and (CH$_3$)$_2$NH$_2$Cl in water. Then, powder sample was obtained by grinding the single crystal in a mortar for one minute and nano-sized powder sample with average particle size of about 7 nm was made using commercial Fritsch planetary ball-mill for about 60 hours. Magnetization measurements were performed down to the lowest temperature of 0.5 K using commercial Quantum Design MPMS-7T equipped with homemade $^3$He refrigerator insert.
3. Result and Discussion

Typical examples of temperature dependent behaviors are presented for powder and nano-sized powder samples in Figure 2 (a) and (b), respectively. As easily noticed, no clear differences can be seen between them. At 0.1 T, the temperature dependence of magnetization \(M(T)\) increases gradually down to about 1.0 K and then it indicates maxima, corresponding to the critical temperature \(T_c\) of SMO phase, before showing abrupt decreasing. At 1.0 T, \(M(T)\) shows almost temperature independent behavior below about 0.8 K in both samples. Such change between 0.1 T and 1.0 T is a consequence of spin-flop transition where the magnetic susceptibility changes from parallel to perpendicular one. Therefore we assigned the \(T_c\) at 1.0 T by extrapolating the two straight lines from low and high temperature sides as indicated in the inset of Figure 2(a). Estimated \(T_c\)'s from these \(M(T)\) measurements are plotted in Figure 1.

In nano-sized sample, no anomalies could be detected at around 1.5 K in low field range below about 3.0 T, even though it is expected from the results of specific heat measurements. In addition, in the high magnetic field range above 3.0 T, we could not obtain any explicit anomalies down to 0.5 K for both samples. The \(M(T)\) shows only gentle temperature dependence in whole temperature range we measured. These results may be understood by considering the following reason. The phase boundaries determined by our previous specific heat studies for both samples are almost parallel to the magnetic field axis, that is, the slope of phase boundary is almost zero. In general such situation occurs at the summit of conventional FIMO phase where the \(M(T)\) does not accompanied by the magnetization change at crossing the phase boundary[9]. Similar situation can be applicable to the whole field range of FIMO phase for nano-sized sample or high field range for powder sample and therefore no anomalies can be detected.

Next we move on to the results of magnetization process \(M(H)\) performed at low temperature of 530 mK for both samples. In the powder sample, the \(M(H)\) increases rapidly to reach the magnetization plateau with 0.5 \(\mu_B\) at around 2.5 T and then increases again gradually above about 4.0 T as shown in Figure 3(a). From the field derivative \(dM/dH\), the spin-flop transition \(H_S F\) can be recognized between about 0.4 T and 1.2 T. Relatively wide field range of transition is attributable to the powder sample with random orientations. In the high field range above

![Figure 2](image-url)
Figure 3. (a) Magnetization $M(H)$ and its field derivative $dM/dH$ curves for powder sample (○) and ball-mill powder sample (●) observed at 530 mK. Two vertical dotted lines denote the spin-flop region. (b) Difference $\delta M(H)$ between $M(H)$ curves for both samples.

3 T, the $dM/dH$ shows gradual change without any clear anomalies as a function of external magnetic field. This is consistent with the $H$-$T$ phase diagram where no phase boundaries are expected in such low temperature.

Result in the nano-sized sample seems to be almost identical to the powder sample. However a definitive difference can be also seen between them. The magnetization plateau is no longer visible in the nano-sized powder indicating the disappearance of spin gap. In Figure 3(b), the difference $\delta M(H)$ between powder and nano-sized powder are also plotted. The $\delta M(H)$ has a complicated field dependence, which is not reproduced by a simple monotonic function such as the Brillouin function expected for the paramagnetic species for example. We think that created extra spins, which should be end-spins on the surface of small particles, in the nano-sized powder influences to the host part strong enough to collapse the spin gap and modify the phase diagram drastically. This is most important result in the present study.

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