Magnetic Phase Diagram of DMA CuCl$_3$

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Abstract. Result of specific heat measurements on the single crystal of DMA CuCl$_3$ is presented and compared with previous one obtained for the powder crystal. Possible reason for the marked difference between them is discussed on the basis of competition between critical fluctuation in the magnon BEC process and short correlation length in the powder crystal.

1. Introduction

The title compound DMA CuCl$_3$(DMA=$(\text{CH}_3)_2\text{NH}_2$) has unique magnetic properties. Figure 1 shows the field versus temperature ($H$-$T$) phase diagram determined by the temperature dependence of magnetic specific heat $C^\text{mag}_p(T)$ in fields up to 8 T [1], and magnetization process observed at 500 mK for the powder sample [2]. At low temperatures, two distinct magnetically ordered phases appear, separated by the narrow disordered phase with the magnetization plateau between $H_{c1} = 2$ T and $H_{c2} = 3.5$ T. The spontaneous magnetic ordered (SMO) phase takes place in the low field range below $H_{c1}$, while above $H_{c2}$ the field induced magnetic ordered (FIMO) phase appears in the high field range up to the saturation field of $H_s = 14$ T. So far, previous studies have revealed that the system contains predominant ferromagnetic (F) and antiferromagnetic (AF) intra-dimer interactions $J_F$ and $J_{AF}$ with practically equal magnitude. Both interactions seem to be responsible for the appearance of the SMO and FIMO phases, respectively [3]. The FIMO phase has relatively higher critical temperature and wider field range than those in the SMO phase. Considering $J_F \sim J_{AF}$, this implies that the subcritical interactions that connect dimers magnetically are larger in FIMO phase than in SMO phase. However the magnetic network is still not well understood at the moment.

One may easily notice that the phase boundary of the FIMO phase has quite unusual shape, especially in the vicinity of $H_{c2}$. Usually, the critical temperature $T_c$ decreases with decreasing the field approaching to the $H_{c2}$, while determined phase diagram has opposite trend that the $T_c$ increases with decreasing the field. Even though, it is not so easy to assign $T_c$ uniquely because of the broadness of observed anomalies in the $C^\text{mag}_p(T)$. Before showing our present study, here, to avoid subjective assignment of $T_c$, we estimated an error bar, which was not included in the previous report, as the peak to peak width of temperature derivative of the magnetic specific heat $dC^\text{mag}_p(T)/dT$. Estimated error bars are quite large as expected near the $H_{c2}$. Including
the error bar, however, the behavior of \( T_c \) is still not conventional. Note that this is not the effect of anisotropic \( g \)-tensor because the \( C_p^{mag}(T) \) shows rather sharp peak in high fields above 6 T.

In the present study, we performed specific heat measurements for the single crystal of DMA CuCl\(_3\), to obtain a possible physical interpretation for such unusual \( H-T \) phase diagram observed in the powder sample. Detailed results and brief discussion will be given in the following sections.

2. Experimental
Deep red single crystal of DMA CuCl\(_3\) used in this study was obtained by slow evaporation of 1:1 solution of CuCl\(_2\)2H\(_2\)O and (CH\(_3\))\(_2\)NH\(_2\)Cl in water. It crystallizes in the monoclinic space group C2/c with lattice parameters of \( a = 17.45 \text{ Å}, b = 8.69 \text{ Å}, c = 11.99 \text{ Å} \) and \( \beta = 125.5^\circ \) at room temperature [4]. Specific heat measurements were performed by the heat pulse method in the quasi adiabatic condition, down to 200 mK using the dilution refrigerator and in magnetic fields up to 8 T with fixed direction parallel to the \( c \)-axis. In the following, the lattice contributions are already subtracted from the observed data by assuming \( T^3 \) dependence in the high temperature range.

3. Result and Discussion
Figure 2 shows the temperature dependence of specific heat \( C_{mag}^{s}(T) \) observed for the single crystal. As we have discussed previously, the broad maximum at around 5 K corresponds to low energy excitations due to the presence of \( F \) and AF dimers. Here let us focus on the field dependent behavior of sharp peak reflecting the magnetic ordering. At 0 T, the sharp peak was observed at \( T_c = 0.90 \text{ K} \), which is slightly larger than \( T_c = 0.84 \text{ K} \) in the powder sample. Applying the magnetic field up to 2 T, the peak moves, losing the intensity, to lower temperature, and disappears at 3 T. Further applying the magnetic field, a small peak appears again at 4 T, and then it grows, moving the position to higher temperature, with increasing field up to 8 T. These behaviors are summarized in the \( H-T \) phase diagram as shown in Figure 3, together with results for the powder sample. Following the procedure performed for \( C_p^{mag}(T) \), error bars were also estimated by the peak to peak width of temperature derivative \( dC_{mag}^{s}(T)/dT \) as typically displayed in the inset of Figure 2. The phase boundary of the single crystal has quite natural shape that both ordered phases seem to close at \( H_{c1} \) or \( H_{c2} \) and \( H_s \) at \( T = 0 \), respectively.

There are marked differences between \( H-T \) phase diagrams for the powder and single crystal. For convenience, we define the notation of the critical temperature \( T_c \) for the powder and single
Figure 2. Temperature dependences of magnetic specific heat $C_{\text{mag}}^s(T)$ observed for the single crystal in fields up to 8 T. For clarity, trace in each magnetic field is shifted vertically by 2 J/Kmol. Arrows indicate critical temperatures $T_c$. Typical example of temperature derivative $dC_{\text{mag}}^s(T)/dT$ is shown in the inset. The peak to peak width of $C_{\text{mag}}^s(T)$ is employed as error bar.

Figure 3. The $H$-$T$ phase diagram (●) determined by present specific heat measurements on the single crystal. Vertical dotted lines denote $H_{c1}$, $H_{c2}$ and $H_s$, respectively. Results by $C_{\text{mag}}^p(T)$ and NMR are also shown by the symbols (O ) and (Π), respectively. Drawing curves (-----) and (----) are just guide to the eyes.

crystal as $T_c^p$ and $T_c^s$, respectively. In the SMO phase, $T_c^p$ is slightly lower than $T_c^s$ in the low field range below about 1 T, while $T_c^p$ is higher than $T_c^s$ at around $H_{c1}$. In the FIMO phase, $T_c^p$ is remarkably higher than $T_c^s$ below about 6 T, and above which both $T_c^p$ and $T_c^s$ almost coincide each other.

Among those, we focus on most outstanding difference seen at the vicinity of $H_{c2}$. In the powder crystal, the phase transition seems to be progressing over a rather wide temperature range, as can be recognized by the length of error bar. Because of the powder crystal, first, we should consider the anisotropic effect. Taking no difference of $T_c$ above 6 T into account, the effect of anisotropic $g$-tensor is excluded for the reason as mentioned before. As another candidate, there is a DM interaction, presence of which is in fact predicted by the ESR study [5]. Depending on the field direction to the DM vector, it brings about anticrossing effect between relevant energy levels. Therefore, the DM interaction can affect on the $T_c$ more or less at around level crossing field of $H_{c2}$.

However, this might be also excluded as a main reason because of the following fact. Recently the NMR study was performed for the powder crystal [6]. The temperature dependence of proton nuclear spin relaxation rate $1/T_1$ showed relatively sharp peak or edge structure even at the vicinity of $H_{c2}$. Plotting such anomalies resulted in the $H$-$T$ phase diagram with practically common shape to that obtained by $C_{\text{mag}}^s(T)$, as shown in Figure 3. Only the $H$-$T$ phase diagram deduced from $C_{\text{mag}}^p(T)$ has peculiar shape.

Thus, a simple question arises. In spite of same powder crystal, why the different $H$-$T$ phase
diagrams were obtained by NMR and $C_{mag}(T)$? To account for such inconsistency, we focus on the different sample condition. That is, in the specific heat measurements, we used to mix the powder crystal with Apiezon grease under vigorous stirring to achieve the good thermal contact. This process may cause the dissolve of powder particle in the grease, leading to a possible disorder or percolation in the mesoscopic scale. There is no direct evidence for such effect, yet we can offer a circumstantial evidence that the $C_{mag}(T)$ lose the intensity compared with $C_{mag}(T)$ even at 0 T, where no difference should be fundamentally observed between them, as shown in Figure 4.

![Figure 4.](image)

**Figure 4.** Difference between $C_{mag}(T)$ and $C_{mag}(T)$ at 0 T, plotted by (●) and (○), respectively. Note that much reduction of intensity occurs in $C_{mag}(T)$ at around $T_c$ and broad maximum, where large entropy is consumed.

In addition, it should be noted that the peak temperature of broad maximum is also decreasing slightly in the $C_{mag}(T)$. This indicates that some change is introduced in the spin system of powder crystal, such as weakening of magnetic correlation. In this course, one possible scenario comes to mind. That is, in the two dimensional granular superconducting film, or even in the bulk high-$T_c$ superconductor, spreading of a critical regime is observed above $T_c$ if the superconducting correlation length is comparable to the thermal fluctuation [7]. In such situation, the phase transition smears out and changes into a crossover phenomenon. By analogy with this, we expect a similar effect for the present case. The field induced magnetic ordering process can be explained by the context of magnon Bose-Einstein condensation [8]. Then, at the vicinity of $H_{c2}$, strong quantum fluctuation may cause blunt critical behaviors as observed in the $C_{mag}(T)$ if the shortening of magnon correlation length is realized in the system.

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