Magnetic Field dependence of specific heat in Clinoatacamite Cu$_2$Cl(OH)$_3$

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Abstract. We have measured the magnetic field dependence of the specific heat up to $H=6$ T in a geometrically frustrated magnet, clinoatacamite Cu$_2$Cl(OH)$_3$, with the corner-sharing tetrahedron structure of the Cu$^{2+}$ ions. At $H=0$ T, the specific heat exhibits two anomalies at $T_1=6.2$ K and at $T_2=18.1$ K. $T_1$ shows a reentrant behavior in the $T-H$ phase diagram, while $T_2$ shows a gradual decrease with increasing magnetic fields. The field dependence of $T_1$ and $T_2$ may reflect different aspects of two transitions. The transition at $T_1$ is related with the two dimensional nature of the kagome antiferromagnets which are weakly coupled via Cu$^{2+}$ ions at the triangular sites located in between the kagome layers, while that at $T_2$ represents the feature in a conventional long-range ordering.

1. Introduction
Magnetic properties in geometrically frustrated systems have attracted much attention for a long time because of their novel features as observed in triangular lattice antiferromagnets. After the proposal of the resonating-valence-bond(RVB) state as a possible ground state for the two-dimensional triangular antiferromagnet by Anderson [1], the experimental observation of quantum spin-liquid ground states such as RVB state has become a central issue in the field of frustrated magnets with quantum spin. Moreover, after the discovery of Haldane gap [2], the RVB and valence-bond-solid (VBS) states are discussed in possible ground states in highly frustrated quantum magnets [3].

Zheng et al., reported characteristic features in clinoatacamite, a geometrically frustrated system of mineral Cu$_2$Cl(OH)$_3$, with the spin structure of the corner sharing tetrahedron of Cu$^{2+}$ ions [4]. It has a monoclinic structure with the lattice constant $a=6.157\text{Å}$, $b=6.814\text{Å}$, $c=9.104\text{Å}$ and $\beta=99.65$. A small antiferromagnetic anomaly due to a long-range magnetic ordering is observed at $T_2=18.1$ K in the specific heat with a small entropy change of about 0.1ln2/Cu. Moreover, the sharp peak of the specific heat is observed at $T_1=6.2$ K. It is verified from $\mu$SR
experiments that the long-range magnetic ordering appearing at $T_2=18.1$ K transforms into a coexisting state of long range ordering and spin fluctuations [5]. The coexistence persists down to $T=20$ mK which is the lowest experimental accessible temperature.

It is considered that the low temperature properties in clinoatacamite are connected with that in herbertsmithite $\text{ZnCu}_3\text{Cl}_2(\text{OH})_6$, in which nonmagnetic Zn$^{2+}$ ions are substituted for Cu$^{2+}$ ions forming the triangular lattice in the corner sharing tetrahedron structure [6]. It is noted that herbertsmithite is considered as a structurally perfect $S=1/2$ kagome antiferromagnet. In herbertsmithite, therefore, the spin structure consists of the stacking of the kagome lattice with $S=1/2$ Heisenberg spin separated by nonmagnetic Zn layers. In fact, the experimental studies on herbertsmithite suggest the appearance of the spin-liquid ground state. The inelastic neutron scattering reveals a spectrum of low energy excitations with no observable gap and the specific heat at very low temperatures follows the power-low dependence [7]. Moreover, the absence of the structural deformation in X-ray diffraction experiments implies that the VBS state is ruled out as the ground state [8].

We have studied the magnetic dependence of the specific heat in clinoatacamite. In the previous paper, we suggested from a small increase of $T_1$ by magnetic fields that the spin fluctuation below $T_1$ in clinoatacamite may be related with the two dimensional (2D) nature of the weakly coupled kagome layers via Cu$^{2+}$ ions at the triangular sites [9]. To further study the 2D nature in clinoatacamite, we pursue the detailed magnetic-field dependence of $T_1$ and $T_2$ by the specific heat measurements up to $H=6$ T.

2. Experimental
Clinoatacamite was prepared using a solution reaction from Cu(HCOO)$_2$·4H$_2$O and KCl in purified water. Polycrystalline clinoatacamite precipitates were thoroughly washed and filtered. The crystalline nature was further improved by a hydrothermal treatment at 200$^\circ$C [4]. The specific heat measurements was performed by a heat pulse method using a $^3$He refrigerator, and a dilution refrigerator below 2 K. Apiezon N grease was mixed with the powdered sample to ensure good thermal conductivity between the sample and the thermometer.

3. Results and Discussion

![Figure 1](image)

**Figure 1.** The temperature dependence of the specific heat in clinoatacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$ at $H=0$, 2, 4 and 6T.

Figure 1 shows the overall feature of the specific heat below $T=20$ K at $H=0$, 2, 4 and 6T. $\lambda$-shaped anomaly at $T_1 \sim 6$ K corresponds to the transition from the antiferromagnetic ordering
state to the coexistence state. As the temperature is decreased, the specific heat decreases rapidly from $\sim 10 \ (J/mol \ K)$ at $T=6$ K to $\sim 0.0015\ (J/K \ mol)$ at $T=150 \ mK$, which is probably caused by the development of the energy gap triggered by the antiferromagnetic ordering detected in the deuterated Cu$_2$Cl(OD)$_3$ by neutron scattering experiments [10]. As the magnetic field is increased, the $\lambda$-shaped anomaly at $T_1$ is suppressed and changes to a round shape. In contrast, the remarkable change of the specific heat cannot be observed at around $T_2$.

In order to observe the field dependence of $T_1$ more closely, we plot the detailed magnetic-field dependence of the specific heat in Fig. 2(a), where the specific heat for $4 \ K \leq T \leq 8 \ K$ is enlarged. A reentrant behavior of $T_1$ is clearly seen. As the magnetic field is increased, the transition temperature at $T_1=6.23 \ K$ in zero field shifts to higher temperatures with decreasing the peak height, and has a maximum $T=6.48 \ K$ at $H=1 \ T$. Above $H=1 \ T$, on the other hand, the peak temperature decreases gradually with increasing magnetic field. We display the $T-H$ phase diagram of $T_1$ in Fig. 2(b). The reentrant field dependence of $T_1$ is in good agreement with the field induced variation of the transition temperature in weakly coupled 2D Heisenberg antiferromagnets [11]. Therefore, it is likely that the transition at $T_1$ reflect the development of the antiferromagnetic ordering in the 2D kagome layers which are weakly coupled via Cu$^{2+}$ ions at the triangular sites located in between the kagome layers as pointed out in the previous paper.

Figure 2. (a) The detailed magnetic-field dependence of the specific heat at around $T_1$. (b) $T-H$ phase diagram of the phase transition at $T_1$.

It is seen from the specific heat below $H=1 \ T$ in Fig. 2(a) that only the sharp peak at around $T_1$ is suppressed with increasing magnetic fields, while a broad hump with a minimum at around $T=6.2 \ K$ is not affected by the magnetic field. These results suggest that the sharp peak at around $T_1$ exhibiting the 2D nature is superposed on the broad hump resulting from the energy gap developed by the antiferromagnetic ordering.

Also, the temperature dependence of the specific heat would be explained by assuming the superposition of two components; the specific heat with the 2D nature and the gapped one. Generally, the specific heat in 2D Heisenberg antiferromagnet shows a power-law temperature dependence. However, the present result does not exhibit a power-law dependence although the 2D nature is confirmed by the reentrant behavior. The fraction following the 2D nature is very small, preventing the observation of the power-law behavior. The superposition of two components in the specific heat may be related with the coexistence of the two states observed in
the µSR experiments. We need further investigation to clarify the characteristic features below $T_1$.

We plot the magnetic field dependence of the specific heat up to $H=6$ T in Fig. 3(a), where the data are shifted by 2 (J/K mol). To see the field dependence of $T_2$, we depict the $T-H$ phase diagram in Fig. 2(b). No reentrant behavior is observed in the field dependence of $T_2$, which is contrary to that of $T_1$. This represents that the transition at $T_2$ is caused by a conventional long range ordering, which is consistent with µSR experiments.

![Figure 3](image_url)

**Figure 3.** (a) The magnetic field dependence of the specific heat, where the data are shifted by 1 (J/K mol). (b) $T-H$ phase diagram of the phase transition at $T_2$

4. Conclusion

We have measured the magnetic field dependence of the specific heat in a geometrically frustrated magnet clinoatacamite with the corner-sharing tetrahedron structure. At $H=0$ T, the specific heat exhibits two anomalies at $T_1=6.2$ K and at $T_2=18.1$ K. $T_1$ shows a reentrant behavior in the $T-H$ phase diagram, while $T_2$ shows a gradual decrease with increasing magnetic fields. The field dependence of $T_1$ and $T_2$ may reflect different aspects of two transitions. The transition at $T_1$ is related with 2D nature of the kagome antiferromagnets which are weakly coupled via Cu$^{2+}$ ions at the triangular sites located in between the kagome layers, while that at $T_2$ represents the feature in a conventional long-range ordering.

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