Specific Heat Study of Geometrically Frustrated Magnet Clinoatacamite Cu\textsubscript{2}Cl(OH)\textsubscript{3}

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Abstract. We have performed the specific heat study in a new geometrically frustrated system, clinoatacamite Cu\textsubscript{2}Cl(OH)\textsubscript{3} with the corner-sharing tetrahedron structure of the Cu\textsuperscript{2+} ions with S=1/2 Heisenberg spin. At H=0 T, two anomalies are observed at T\textsubscript{1}=18.1 K and at T\textsubscript{2}=6.2 K. The specific heat decreases rapidly below T\textsubscript{2} and shows no anomaly down to T=150 mK despite the existence of the spin fluctuation shown in the \(\mu\)SR experiments. As the magnetic field is increased, the sharp peak at T\textsubscript{2} is broadened and shows a small reentrant behavior in the T−H phase diagram. On the other hand, the peak at T\textsubscript{1} shows no obvious change up to H=5 T. The entropy at T\textsubscript{1} is estimated as \(\sim 0.35R\ln2\) at H=0 T. These features may be caused by the two dimensional nature of the kagome antiferromagnets which are weakly coupled via Cu\textsuperscript{2+} ions at the triangular sites located in between the kagome layers.

1. Introduction

Magnetic properties in low-dimensional quantum spin systems have attracted much attention for a long time because of their novel features. Since the proposal of the resonating-valence-bond (RVB) state as a possible ground state for the two-dimensional triangular antiferromagnet by Anderson [1], a lot of theoretical and experimental works have been devoted to study the quanum spin-liquid ground state. Moreover, after the discovery of the high temperature superconductivity, the RVB state is discussed in connection with the mechanism of the superconductivity [2].

It is reported that ZnCu\textsubscript{3}Cl\textsubscript{2}(OH)\textsubscript{6} known as herbertsmithite is a structurally perfect S=1/2 kagome antiferromagnet [3]. In herbertsmithite, nonmagnetic Zn\textsuperscript{2+} ions are substituted for Cu\textsuperscript{2+} ions forming the triangular lattice in the corner sharing tetrahedron structure. 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 suggests the appearance of the spin-liquid ground 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 with \(\alpha T\) where \(\alpha \leq 1\) [4].

Zheng et al., reported characteristic features in clinoatacamite Cu\textsubscript{2}Cl(OH)\textsubscript{3} [5]. The spin structure of clinoatacamite has a corner sharing tetrahedron of a monoclinic crystal system with
the lattice constant $a=6.157\text{Å}$, $b=6.814\text{Å}$, $c=9.104\text{Å}$ and $\beta=99.65^\circ$ [6]. Hence, in clinoatacamite the kagome layers are weakly coupled via Cu$^{2+}$ ions at the triangular sites located in between the Cu$^{2+}$ kagome layers. In the susceptibility measurements, two anomalies due to antiferromagnetic (AF) transitions are observed at $T_1 \sim 18$ K and at $T_2 \sim 6$ K. $\mu$SR experiments revealed that the anomaly at $T_1$ corresponds to the conventional phase transition from the paramagnetic state to the AF long-range ordering one, while the AF ordering state appearing at $T_1$ changes into a unconventional state at $T_2$ where partial long-range magnetic ordering and spin fluctuation coexist [5]. Moreover, the coexistence persists down to $T=20$mK.

From the analogy to the spin structure in ZnCu$_3$Cl$_2$(OH)$_6$, the spin fluctuation below $T_2$ 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 [7]. To study the intriguing properties in clinoatacamite from the viewpoint of a weakly coupled 2D magnet, we performed specific heat measurements up to $H=5$ T. Our results may be explained by the 2D nature of the kagome antiferromagnet which are weakly coupled via Cu$^{2+}$ ions. It is surprising that the specific heat drops by nearly four orders, from $\sim$10 (J/mol K) at $T=6$ K to $\sim$0.0015 (J/K mol) at $T=150$ mK despite the existence of the spin fluctuation confirmed in the $\mu$SR experiments.

2. Experimental
The sample preparation is given in ref. 6. The specific heat measurements was performed by a heat pulse method using a $^3$He refrigerator and a dilution refrigerator. Apiezon N grease was mixed with powdered sample to ensure good thermal conductivity between the sample and the thermometer.

3. Results and Discussion
The temperature dependence of the specific heat is plotted in Fig. 1. Two anomalies are observed in the specific heat at $T_1=18.1$ K and at $T_2=6.2$ K. The anomaly at $T_1$ is quite small and the specific heat below $T_1$ decreases slowly with decreasing temperature. Also, a subtle anomaly appears at $T_1$ in the susceptibility. These suggest that the spins are not frozen completely at $T_1$.

![Figure 1](image.png)

**Figure 1.** (a) The temperature dependence of the specific heat in clinoatacamite Cu$_2$Cl(OH)$_3$. The inset is shown in the low temperature region. (b) The temperature dependence of the magnetic entropy at $H=0$ T and 5 T.
According to the $\mu$SR study, the $\lambda$ shaped anomaly at $T_2=6.2$ K is the transition from the AF ordering state to the coexisting state. The low-temperature specific heat below $T=2$ K is depicted in Fig. 1. No anomaly due to the magnetic ordering is observed down to $T=150$ mK, although the spin fluctuation is confirmed at $T=20$ mK in the $\mu$SR. $T^2$-dependence of the specific heat due to the spin wave excitation is expected in the AF ordering below $2/3$ of the critical temperature. However, the results below $T=4$ K are clearly inconsistent. This is likely caused by the development of the energy gap triggered by the AF ordering observed in the deuterated Cu$_2$Cl(OD)$_3$ in neutron scattering experiments [7]. The energy gap appears at around $\hbar\omega=1$ meV at $T=6$ K. Moreover, $\hbar\omega$ increases with decreasing temperature. The energy gap causes the exponential temperature dependence of the specific heat, leading to the characteristic temperature dependence below $T_2$.

Also, the emergence of the energy gap is supported by the value of the specific heat at the lowest temperatures. The value drops by nearly four orders, from $\sim10$ (J/mol K) at $T=6$ K to $\sim0.0015$ (J/K mol) at $T=150$ mK, suggesting the existence of a large energy gap. In atacamite which is the polymorphs of clinoatacamite with the spin structure of the corner sharing tetrahedron, the AF ordering occurs at $T=9$ K. The temperature dependence of the specific heat below $T_N$ is rather mild compared to that in clinoatacamite. The value at $T=150$ mK is $C\sim0.02$ (J/K mol), which is an order larger than that of clinoatacamite [8]. In ZnCu$_3$Cl$_2$(OH)$_6$, the specific heat below $T=1$ K shows a power low temperature dependence $C=\gamma T^\alpha$ where $\alpha \leq 1$. The value at $T=150$ mK is reported to be $C\sim0.1$ (J/mol K), which is much larger than that in clinoatacamite [4].

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) The magnetic field dependence of the specific heat at representative fields. (b) The enlargement of the specific heat at around $T_2$. The absolute values are shifted for eyes.

The magnetic field dependence of the specific heat is shown in Fig. 2(a). It is seen that the sharp peak at $T_2$ collapses into a broad peak with increasing magnetic field. The enlargement below $T=10$ K is shown in Fig. 2(b). It is important that the reentrant behavior of $T_2$ is seen in the $T-H$ phase diagram. The AF transition moves to higher temperatures gradually from $T_2=6.2$ K at $H=0$ T to 6.5 K at $H=1$ T, while the maximum of the peak shifts to lower temperatures at higher fields. This field dependence of $T_2$ is in agreement with the field induced variation of the AF transition temperature in weakly coupled 2D Heisenberg antiferromagnets [9]. The transition at $T_2$ would reflect the development of the AF ordering in the kagome layers.
On the other hand, the AF transition temperature $T_1$ is almost the same up to $H=5$ T. In this case, the exchange field for the transition is considered to be much larger than the external field of $H=5$T, thus leading to no clear variation.

By subtracting the lattice contribution with $T^3$-dependence which is estimated from the high temperature specific heat above $T_1$, the temperature dependence of the specific heat is obtained as depicted in Fig. 1(b). Only 35% of the magnetic entropy $R\ln 2$ is consumed at $T_1$. Moreover, the magnetic field up to $H=5$ T does not modify the consumption of the magnetic entropy at $T_1$, suggesting no residual entropy at lower temperatures. The magnetic entropy $(1-0.35)R\ln 2$ is considered to be released at higher temperatures above $T_1$. Similar features are observed in the magnetic ordering for low-dimensional magnetic systems in which the magnetic entropy released below the phase transition is lower than $0.5R\ln 2$ [9, 10]. In the 1D and 2D magnetic systems, the spin fluctuation is suppressed by the intrachain or intralayer exchange interaction at higher temperatures, and freezes at 3D magnetic ordering temperature due to a weak interchain or interlayer interaction. In the kagome AF magnet ZnCu$_3$Cl$_2$(OH)$_6$ with the Weiss temperature $\theta \sim -300$ K, the exchange interaction is reported to be $J \sim 190$ K. This suggests a large value of the antiferromagnetic exchange interaction $J$ for the kagome layer in clinoatacamite with $\theta \sim -200$ K whose susceptibility shows the similar behavior at higher temperatures with that in ZnCu$_3$Cl$_2$(OH)$_6$.

4. Conclusion

We have performed the specific heat study in a new geometrically frustrated system, clinoatacamite Cu$_2$Cl(OH)$_3$ with the corner-sharing tetrahedron structure of the Cu$^{2+}$ spins. The H-T phase diagram of the lower transition at $T_2$ shows a small reentrant behavior to the magnetic field. The magnetic entropy below the AF transition is estimated as $\sim 0.35R\ln 2$ at $H=0$ and 5 T. The rest is considered to be released at higher temperatures. These features may reflect the 2D nature of the kagome antiferromagnets which are weakly coupled via Cu$^{2+}$ ions at the triangular sites located in between the Cu$^{2+}$ kagome layers.

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