NMR study of pyrochlore lattice antiferromagnet, melanothallite Cu$_2$OCl$_2$

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Abstract. The melanothallite Cu$_2$OCl$_2$ is a new example of pyrochlore-like antiferromagnet, which is composed of 3d transition metal electrons. We performed Cu- and Cl-NMR experiments on powder samples of Cu$_2$OCl$_2$ below transition temperature $T_N = 70$ K and we observed six resonant peaks of Cu nuclei, which are composed of three symmetric peaks corresponding to $^{63}$Cu and three corresponding to $^{65}$Cu. The Cu nuclei feel the strong hyperfine fields because of ordered magnetic moments and the electric field gradients. We determined the spin structure by analyzing the Cu-NMR spectra. The melanothallite has an all-in-all-out spin structure. The spin lattice relaxation rates $T_1^{-1}$ of Cu- and Cl-NMR in the ordered phase are proportional to the temperature; This suggests that although long-range ordering occurs at rather high temperature, the large spin fluctuations caused by the geometrical frustration still remain.

1. Introduction
The pyrochlore lattice is composed of corner-sharing tetrahedra. The antiferromagnet on the pyrochlore lattice with nearest neighbour Heisenberg interactions has the macroscopic number of degeneracy and has no long-range magnetic ordering even at zero temperature. This magnetic tetrahedron system has attracted much interest because of three-dimensional geometrical frustration. A well-known example is an $A_2B_2O_7$ system, in which $A$ is a rare earth element and $B$ is a 3d-transition metal element. In these compounds 4f-electrons dominate their magnetic properties and their main interaction is a long-range dipolar interaction. In contrast, the interaction in the 3d-electron system is short-range exchange interaction. Thus, the 3d-electron antiferromagnets on the pyrochlore lattice are considered to be simpler than 4f-electron pyrochlore antiferromagnets. Recently, clinoatacamite Cu$_2$(OH)$_3$Cl with $s = 1/2$, atacamite Ni$_2$(OH)$_3$Cl with $s = 1$, Cu$_3$O$_4$ with $s = 1/2$, and FeF$_3$ with $s = 5/2$ have been reported to be pyrochlore-like antiferromagnets with 3d-electron system [1–3]. These compounds were reported to show interesting behaviours, such as successive transitions, exotic critical behavior, large spin fluctuation in the spin-freezing phase, and novel spin structure in the ordered phase. These behaviors are considered to be due to additional perturbations, such as further neighbouring interactions, anisotropies, or a lattice distortions [1–5]. The melanothallite is a new example of the pyrochlore-like antiferromagnet with the 3d-electron system.
Figure 1. Crystal structure of melanothallite. The blue, red, and green balls represent copper, oxygen, and chlorine, respectively. The thick blue bonds between \( \text{Cu}^{2+} \) represent the exchange interaction \( J \), and the thin ones represent the exchange interaction \( J' \). The tetrahedra composed of Cu are shown in yellow. The figures was prepared using the VESTA program [6].

The crystal structure of melanothallite is orthorhombic, as shown in figure 1, and its space group is \( Fdd\bar{d} \). The lattice constants are \( a = 9.542 \text{ Å}, b = 9.712 \text{ Å}, \) and \( c = 7.396 \text{ Å} \). All \( \text{Cu}^{2+}, \) \( \text{O}^{2-} \) and \( \text{Cl}^{-} \) belongs crystallographically to corresponding identical sites. The magnetic ion \( \text{Cu}^{2+} \) has a spin of \( 1/2 \). The oxygens are located at the centre of the tetrahedra composed of \( \text{Cu}^{2+} \). These tetrahedra form the pyrochlore lattice by the corner-sharing network of \( \text{Cu}^{2+} \). On the other hand, the crystal structure could be considered to be composed of the vertical cross-stacking of one-dimensional chains of \( \text{Cu}^{2+} \), as shown in figure 1 by the thick blue bonds. The super-exchange path between Cu moment that consists \( \text{Cu}–\text{O}–\text{Cu} \) and \( \text{Cu}–\text{Cl}–\text{Cu} \) is represented by thick blue line. Thin blue line represents the super-exchange \( \text{Cu}–\text{O}–\text{Cu} \) path. Controversy had existed on whether this compound should magnetically be considered a three-dimensional pyrochlore lattice or a one-dimensional chain.

The temperature dependence of susceptibility shows a broad peak at about 140 K and an antiferromagnetic ordering at \( T_N = 70 \text{ K} \) [7]. The broad maximum cannot be explained by a one-dimensional antiferromagnetic model with only intrachain interactions \( J \). If a modified one-dimensional model with intrachain interactions \( J \) and interchain interactions \( J' \), as shown in figure 1, is assumed, the fitting can be improved. However, the obtained \( J \) and \( J' \) are 113 K and 108 K, respectively, and thus they are nearly the same [7]. Therefore the one-dimensional model is not appropriate, and it is suggests that the melanothallite, \( \text{Cu}_2\text{OCl}_2 \), is a slightly distorted pyrochlore lattice antiferromagnet.

The specific heat measurement also indicates that the long-range magnetic ordering occurs below \( T_N = 70 \text{ K} \) [7]. At temperature below \( T_N \), the clear muon spin precession signals were observed in the \( \mu \text{SR} \) measurement in the long-range ordered phase [8]. However, the time spectra of the \( \mu \text{SR} \) measurement show exponential damping even below \( T_N \), which suggests that spin fluctuations still exist even below \( T_N \) because of the geometrical frustration [8]. The spin structure and the origin of large spin fluctuation in the ordered phase have not been determined.
Therefore we have investigated the spin structure and spin fluctuations of the new 3d-electron pyrochlore antiferromagnet, Cu$_2$OCl$_2$, microscopically by nuclear magnetic resonance (NMR) measurement.

2. Experiment
We have performed Cu- and Cl-NMR experiments on polycrystalline samples of Cu$_2$OCl$_2$. The sample was synthesized by a conventional solid-state reaction of high-purity CuCl$_2$ and CuO powders. The stoichiometric powder mixtures were pressed into pellets and sintered at 623 K for 18 h in CO$_2$ flow.

The spin-echo spectra of $^{63}$Cu ($I = 3/2$), $^{65}$Cu ($I = 3/2$) and $^{35}$Cl ($I = 3/2$) was obtained and the spin-lattice relaxation rates $^{63}T_{1}^{-1}$ of $^{63}$Cu and $^{35}T_{1}^{-1}$ of $^{35}$Cl were obtained using a coherent phase spectrometer. The spectra of Cu nucleus were obtained by a frequency sweep without an external magnetic field. In the case of the Cl-NMR, the spectra were obtained by a field sweep at an operating frequency of 24.08 MHz. No magnetic field was applied for the measurements of the relaxation rates of the Cu nuclei.

3. Experimental Results and Discussions
The Cu spin-echo spectra at $T = 2.9$ K below $T_N$ without external magnetic field is shown in figure 2. Six sharp resonant peaks were clearly observed; three equally-spaced peaks corresponding to $^{63}$Cu nucleus and three equally-spaced peaks corresponding to $^{65}$Cu nucleus. The three symmetric peaks for each Cu nucleus are due to the internal magnetic field and the electric field gradient (EFG). These resonant peaks can be analyzed on the basis of the Zeeman interaction and electric quadrupole interactions. The Hamiltonian of Cu nucleus is expressed as

$$\mathcal{H} = \frac{eQV_{zz}}{4I(2I-1)} \left[ 3I_z^2 - I^2 \right] + \frac{\eta}{2} \left( I_+^2 + I_-^2 \right) + \gamma \hbar H_{\text{local}} I_z',$$

Figure 2. Cu-NMR spectrum at $T = 2.9$ K below $T_N$ with no external magnetic field. The blue and green solid arrows indicate $^{63}$Cu, and $^{65}$Cu peaks, respectively.
Table 1. Values of center-peak frequencies $f_c$, local fields at Cu site $H_{\text{local}}$, and NQR frequencies $\nu_Q$, and modified EFG $\nu_Q/Q$.

| nucleus | $f_c$ (MHz) | $H_{\text{local}}$ (T) | $\nu_Q$ (MHz) | $\nu_Q/Q$ ($10^{24}$ MHz/cm$^2$) |
|---------|------------|-----------------|--------------|-------------------------------|
| $^{63}\text{Cu}$ | 112.2 | 9.94 | 25.2 | 119.4 |
| $^{65}\text{Cu}$ | 120.2 | 9.94 | 23.5 | 120.5 |

$^{63}\text{Cu}$: $\gamma_{63}=11.285$ (MHz/T) and $Q_{63}=-0.211$ ($10^{24}$ cm$^2$).
$^{65}\text{Cu}$: $\gamma_{65}=12.089$ (MHz/T) and $Q_{65}=-0.195$ ($10^{24}$ cm$^2$).

where $I_z$, $I_+$ and $I_-$ are the nuclear spin operators; $Q$ is the nuclear quadrupole moment; $\gamma$ is the gyromagnetic ratio; and $H_{\text{local}}$ is the magnetic local field at the Cu nucleus position. The second-order derivatives of the electric potential $V_{\alpha\alpha} = \partial^2 V/\partial \alpha^2$ ($\alpha = x, y, z$) denote components of the EFG tensor in the principal coordinate system with $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, and $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetric parameter. The principal axis $z$ of the EFG is generally not along the direction of the localized magnetic field $z'$. The nuclear quadrupole resonant (NQR) frequency $\nu_Q = eQV_{zz}/4I(2I - 1)\hbar$ is a measure of size of the EFG, and the value of $\nu_Q$ is experimentally determined by measuring half the distance between the two satellite peaks. The values of $\nu_Q$ are obtained from the spectra of $^{63}\text{Cu}$ and $^{65}\text{Cu}$ in figure 2, and these values are presented in table 1. The value of the centre peak frequencies $f_c$ are obtained from the spectra in figure 2, and these values are listed in table 1.

The NQR frequency $\nu_Q$ is a quarter of the $f_c$, as is seen in table 1. Thus the electric quadrupole interaction is too large to be treated as a perturbation for Zeeman interaction. In this case, the shift of the spectra becomes asymmetrical depending on the angle between the principal axis $z$ of the EFG and the principal axis $z'$ of the local magnetic field. The obtained Cu-NMR spectra are symmetric, which implies that the axis $z$ and axis $z'$ are parallel. The local magnetic fields $H_{\text{local}}$ are obtained from the centre-peak frequencies $f_c$ by $H_{\text{local}} = f_c/\gamma$, and are listed in table 1. For convenience, the modified EFG are determined as $\nu_Q/Q = eV_{zz}/4I(2I - 1)\hbar$, and these values are listed in table 1. The values of $\nu_Q/Q = eV_{zz}/4I(2I - 1)\hbar$ and $H_{\text{local}}$ depend only on the environment around the Cu nucleus and not on kinds of isotope nucleus. The modified EFG $\nu_Q/Q$ and the local field $H_{\text{local}}$ at all Cu nucleus positions are found to be identical, as seen in from table 1. In addition, since the obtained spectra are very sharp, $H_{\text{local}}$, $\nu_Q/Q$, and the angle between the principal axes $z$ and $z'$ have no distribution. We find that the EFG, the magnetic moment of Cu spin, and the angle between the principal axis $z$ of the EFG and the principal axis $z'$ of the local magnetic field are uniform. This is suggested that the magnetic and crystallographic unit cells are the same.

We calculated the EFG at the Cu site by assuming a point charge on O$^{2-}$ and on Cl$^{1-}$. The direction of $V_{zz}$ at the Cu site is found to be the direction almost from Cu to O that locates the center of tetrahedron. The spin structures that the spin directs toward the center of tetrahedron are, so-called, the 2-in-2-out, 3-in-1-out, and all-in-al-out spin structures. Since the nearest neighbour interaction in Cu$_2$OCl$_2$ is determined to be antiferromagnetic by the susceptibility measurement, the all-in-all-out spin structure is energetically stable. Therefore, the magnetic structures of Cu$_2$OCl$_2$ are the all-in-all-out type, as shown in figure 3.

The ground state of Heisenberg pyrochlore antiferromagnet with only nearest-neighbour interaction $J$ has the macroscopic number of degeneracy even at zero temperature, and has no magnetic long-range ordering. Thus, the observed spin ordering in Cu$_2$OCl$_2$ should be caused by additional perturbative effects. Further neighboring interactions, distorted nearest-neighbour interactions, and the anisotropy are considered to be the additional perturbative effects in Cu$_2$OCl$_2$. First, we consider further neighbouring interactions and distorted nearest-
neighbouring interactions. The case with the additional exchanges of the second-neighbouring interaction $J_2$ and the third-neighbouring interaction $J_3$ were studied by Monte Carlo simulations [4]. The simulations show that the $q = 0$ states are stable. The $q = 0$ states contain the all-in-all-out spin structure and collinear spin arrangement. The collinear spin arrangement is thermally selected due to the entropy effect. In Cu$_2$OCl$_2$, the pyrochlore lattice is slightly distorted with $|J| = 113\,\text{K} > |J'| = 108\,\text{K}$. In this case, the collinear ordered spin arrangement is also energetically favored. Thus, models with $|J| > |J'|$ and further interactions cannot explain the obtained spin structure of Cu$_2$OCl$_2$ in the ordered phase.

Next we consider the effect of the anisotropy. Because the pyrochlore lattice has no inversion centre between the lattice points, it is possible that Dzyaloshinsky-Moriya interactions (DMI) exist in Cu$_2$OCl$_2$. Therefore it is reasonable to discuss the DMI. The DMI are written as $H_{\text{DMI}} = \sum_{\langle ij\rangle} D_{ij} \cdot (S_i \times S_j)$, where $D_{ij}$ is a DMI vector. The ground state of Heisenberg pyrochlore antiferromagnet with DMI has been studied by Monte Carlo simulations [5]. In reference 5, it has been considered to have two types of DMI configurations — direct and indirect DMI. In the pyrochlore lattice, the $D$ vector exists in the vertical plane at the middle point of the edge and is parallel to the opposite side edge. The difference between direct and indirect is the sign of $D$. The direct and indirect DMI lead to the all-in-all-out structure and a collinear ordered spin structure, respectively. Thus the DMI resolve the degeneracy between the all-in-all-out state and collinear ordered states. Since Cu$_2$OCl$_2$ is not an ideal pyrochlore structure and DMI configuration depend on the symmetry of the crystallographic structure, we cannot simply apply this DMI configuration to Cu$_2$OCl$_2$. It is, however, thought that DMI can exist in Cu$_2$OCl$_2$, because Cu$_2$OCl$_2$ has no inversion centre between the Cu$^{2+}$ ions and because the perpendicular bisector at the middle point of the $J$ bond is a mirror plane. It is likely that the DMI in $J$ bond is similar to the direct DMI configuration. Thus, we conclude that the DMI play the important roles on the magnetic ordering and structure in Cu$_2$OCl$_2$.

The rates $^{63}T_1^{-1}$ of $^{63}$Cu were measured at the centre peak that corresponds to $-1/2 \leftrightarrow +1/2$ transition. The temperature dependences of $^{63}T_1^{-1}$ and $^{35}T_1^{-1}$ of $^{35}$Cl are shown in figure 4. The divergent behaviour of the temperature dependence of $^{35}T_1^{-1}$ is observed near $T_N$ as shown in figure 4. This implies that a critical slowing down occurs around $T_N$. We found that both rates in the ordered phase are proportional to the temperature, $T_1^{-1} \propto T$. When the spin-wave excitation is dominant in the long-range ordered spin system, the $T_1^{-1}$ exhibits an approximately a power-like-law dependence on temperature, $T^{-\alpha}$ where $\alpha > 2$. The results for $T_1^{-1}$ may suggest that although the long-range ordering occurs at rather high temperature, the large spin fluctuations caused by the geometrical frustration still remain. These results are consistent with the results of the $\mu$SR results.

In summary, we performed the NMR study of the 3d-electron pyrochlore antiferromagnet Cu$_2$OCl$_2$. Based on the analysis of the Cu-NMR spectra, Cu$_2$OCl$_2$ has long-range ordering.
Figure 4. Temperature dependence of spin-lattice relaxation rates, $^{35}T_1^{-1}$ of $^{35}$Cl and $^{63}T_1^{-1}$ of $^{63}$Cu. Red squares represent $^{35}T_1^{-1}$, and blue circles represent $^{63}T_1^{-1}$. The dashed line indicates $T_N$. The rate $^{63}T_1^{-1}$ was measured under the external field of 57.7 kOe at an operating frequency of 24.08 MHz. The rate $^{63}T_1^{-1}$ was measured without the external field at the centre peak. The red and blue solid lines represent $T_1^{-1} \propto T$, and the dotted line is a guide for the eye.

below $T_N$. The spin structure of Cu$_2$OCl$_2$ in ordered phase is all-in-all-out type spin structure, and the DMI is a plausible cause for this spin ordering. The temperature dependence of $T_1^{-1}$ suggests that large spin fluctuations exist in the ordered phase.

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