Cu-NMR study of the quasi-one-dimensional magnet \( \text{Cu}_3\text{Mo}_2\text{O}_9 \)

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Abstract. A quasi-one-dimensional spin system \( \text{Cu}_3\text{Mo}_2\text{O}_9 \), which has two spin degrees of freedom, the antiferromagnetic linear chain site and dimer-like site weakly interacting with each other, shows a 3D-antiferromagnetic order at \( T_N=7.9 \) K. We report the result of Cu-NMR on the single crystal of this system both in antiferromagnetic and paramagnetic states. In field-swept spectra, we observe two types of signals, which come from the chain site and the dimer-like site, respectively. With increasing resonant frequency, the signal from chain site shifts to lower magnetic field, while that from dimer-like site to higher field. This anomalous behaviour of the chain-site signal is explained in terms of the cancellation between the hyperfine field of about 8.5 T at the chain-site Cu and the applied field. A weak but finite hyperfine field of the dimer-like site indicates that there exists a localized spin on the site, indicating that it is not a singlet state.

1. Introduction

Quantum fluctuation and frustration often bring unexpected effect on the magnetic order of spin system, such as Bose-Einstein condensation of delocalized magnons in three dimensionally coupled antiferromagnetic dimer system[1] or Wigner crystallization in frustrated spin system on the Shastry-Southerland lattice[2]. The subject of this paper is to investigate the effect of the quantum fluctuation and frustration on the spin system that bears two degrees of freedom coupling with each other. Such a bicomponent magnet is represented by \( \text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13} \) that consists of quantum spin dimer and crankshaft-shaped chains of classical spins as previously investigated by Masuda et al.[3] Quite recently another bicomponent magnet \( \text{Cu}_3\text{Mo}_2\text{O}_9 \) attracted much attention, because this quasi-one-dimensional system consists of the two quantum spin components, spin-1/2 linear chain and spin-1/2 dimer-like pair[4,5], coupling weakly with each other. From the intensive study on magnetization and specific heat by Hamasaki et al.[6,7], it has been revealed that a long range magnetic order occurs at \( T_N=7.9 \) K, and that the ordered state is accompanied by a weak ferromagnetism due to Dzyaloshinsky-Moriya interaction. Just below \( T_N \), weak ferromagnetic moments are randomly oriented at zero field, and aligned under a very weak field below 1 T. An anomalous dependence of this weak ferromagnetism and \( T_N \) on the applied field and its direction are reported and argued to be originated in the quantum fluctuation and frustration effect[6,7,8]. However, a spin structure of the two components in this compound has not been established yet. In this paper, we report our NMR study on this compound in the magnetically-ordered and paramagnetic phases from a microscopic point of view.
2. Experimental

Schematics of crystal structure and magnetic bonds are shown in Fig. 1. The space group of the compound is Pnma. There are three crystallographically inequivalent copper sites; Cu1 resides on the linear chain that runs along b-axis, and the other two sites Cu2 and Cu3 locating at slightly inequivalent positions form a dimer-like pair clinging around the chains. There are two chains called α and β connected with a glide symmetry in a unit cell[6]. From analysis on the temperature dependence of magnetic susceptibility, it has been reported that the two antiferromagnetic interactions $J_3$ in the chain and $J_4$ in the dimer are dominant, while the chain-dimer interactions $J_1$ and $J_2$ are very weak. However the effect of $J_1$ and $J_2$ cannot be neglected, because they bring frustration within the tetrahedron formed by two Cu1 atoms in the chain and Cu2 and Cu3 in a dimer.

For the analysis of NMR spectra, the electric field gradient (EFG) tensor at each Cu site was calculated by the point charge model. Reflecting the local symmetry, the principal axis of Cu1 is nearly within $ab$-plane and that of Cu2 and Cu3 lie within $ac$-plane as shown in Fig. 1. Because the principal axis of each pair of Cu sites connected with the glide symmetry is oriented symmetrically around the crystal axes, these glide-pairs are expected to give identical NMR lines as long as the magnetic field is applied along one of the crystal axes.

A single crystal with an approximate size of $2 \times 3 \times 2$ mm$^3$ was prepared by flux method[6]. $^{63/65}$Cu-NMR experiments were performed in a temperature region 3.7-40 K by a conventional spin-echo method using a 12 T cryo-cooled superconducting magnet. Spectra are measured with the resonance frequencies 100-150MHz and in the field directed along either of the three crystal axes a, b and c.

3. Results and Discussion

Figure 2 shows the profile of field-swept spectra measured with various resonance frequencies at 3.7 K, where the system is in the magnetically ordered state. The field direction is parallel with c-axis. We observed four sets of peaks labelled as I-IV. One can clearly see that all the peaks except those belonging to group I shift to higher field with increasing resonance frequency $\omega$. Positions of peaks in group I move contrarily to lower field with increasing $\omega$ and are set back to higher field again when $\omega$ exceeds 125 MHz. The $\omega$ dependence of the position of each peak is shown in Fig. 3. Peaks
belonging to groups II-IV shift linearly with $\omega$ to higher field, and each of them was fitted well with a linear function $H/\gamma + C$ in a measured field range, where $\gamma$ and $C$ are the gyromagnetic ratio of $^{63}\text{Cu}$ (11.285 MHz/T) or $^{65}\text{Cu}$ (12.090 MHz/T) and the constant involving the nuclear electric quadruple interaction and the hyperfine field from the ordered moment, respectively. Mean values of the hyperfine field in groups II, III and IV are roughly estimated from the central position of spectrum to be $+4$, $+2$ and $+0.4$ T, respectively. The observed good linear fitting indicates that the hyperfine field of each peak is independent of the applied field.

The anomalous change in the peak position in group I indicates a cancellation between the applied field and the hyperfine field produced by the ordered moment at one of the two sub-lattices. We assumed the hyperfine field $H_{\text{int}}$ and the electric quadruple parameter $v_0$ of $^{63}\text{Cu}$ as 8.5 T and 38 MHz, and the principal axis of EFG tensor as calculated by the point charge model on Cu1 site, and plotted resonance frequencies of three resonance lines for copper nuclei ($I=3/2$), $\gamma H_{\text{int}} - \gamma H + 3v_0^2/16\gamma H$ and $\gamma H_{\text{int}} - \gamma H + v_0$, calculated by the second-order perturbation, in Fig. 3. One can see that the gray lines reproduce well the observed peaks of group I below 125 MHz. This result gives a direct evidence for the long-range antiferromagnetic order in the chain site Cu1, where the large hyperfine field is produced by the ordered moment at the onsite atom. The observed peaks correspond to the satellite transition $I_z = \frac{3}{2} \leftrightarrow \frac{1}{2}$. Peaks of other transitions are located outside the experimental frequency region. The hyperfine field of 8.3 T is a reasonable value that the ordered moment of 1 $\mu_B$ produces at the onsite divalent copper.

The turnback of the peak position above 125 MHz is explained as the effect of weak ferromagnetism. It has been reported that the weak ferromagnetic moments of approximately 0.005 $\mu_B$ are randomly oriented at 3.7 K in zero field[6], blocking our observation of zero-field NMR signal by producing a random field at Cu1 site. When applying field along c-axis, the weak ferromagnetic moments are aligned and saturate at around 1 T. This is why the peaks of group I can be observed only above 1 T. They were not observed for the case $H//a$-axis, which is consistent with the fact that the alignment of weak ferromagnetic moments does not take place for this field direction[6].

Figure 4 shows the profile of spectrum at various temperatures below and above $T_B \approx 9.6$ K, which is reported to increase from zero-field value of 7.9 K with increasing field ($H//a$) and saturate above 6

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**Figure 3.** Resonance-frequency dependence of observed peaks. Solid (open) symbols and solid (dashed) lines show fitted lines to the peak positions of $^{63}\text{Cu}$ ($^{65}\text{Cu}$) isotope.

**Figure 4.** Profile of Cu-NMR spectra of group IV at various temperatures that straddle $T_N$ at 7.9 K. Vertical lines show the zero shift positions of $^{63}\text{Cu}$ and $^{65}\text{Cu}$.
With increasing temperature, peaks belonging to group IV shift monotonically to higher field without changing spacing between them. Peaks in other groups II and III showed the same behavior. This observation indicates that the peak split within each group is entirely due to the electric quadruple interaction and that the staggered component of the ordered moment contributes none. Consequently, peaks of groups II-IV are considered to come from Cu2 and Cu3, because Cu2 and Cu3 are located at a symmetric position between two adjacent Cu1s in the chain, the staggered component of ordered moment is cancelled out, and only the weak ferromagnetic component contributes to the hyperfine field at Cu2 and Cu3. The fact that the observed hyperfine field in the ordered state is very small also supports this assignment. In the vicinity of $T_N$, the signal intensity rapidly decreases, and the peaks are smeared to become a broad single hump. This gives an evidence of the second-order phase transition at $T_N$, where the critical slowing down of spins gives rise to the transverse nuclear spin relaxation rate $T_2^{-1}$ causing the reduction in the signal intensity and homogeneous broadening. At the temperature 40 K far above $T_N$, a refined structure with many peaks appears again. The number of peaks is larger than the ordered state, because the peaks in the other groups II and III with larger hyperfine fields get merged.

The observed two different types of signals I and II-IV clearly demonstrate that there exist two spin degrees of freedom in this system, the antiferromagnetically ordered chain site and the dimer-like site. The latter is not in a singlet state, because the hyperfine fields of Cu2 and Cu3 are finite and differ from each other. Generally, there are two contributions to the hyperfine field in a magnetically ordered state; one is the onsite moment contribution and the other is the transferred hyperfine field from neighboring spins. In the present case, the chain-dimer interactions $J_1$ and $J_2$ are very weak, so that the effect of the transferred hyperfine interaction is negligibly small compared with the onsite moment contribution. Therefore, the observed hyperfine field of NMR peaks in groups II-IV indicates that a localized moment roughly estimated to be 0.04-0.4 $\mu_B$ may exist at Cu2 and Cu3, where we assumed the onsite hyperfine coupling constant of the Cu site to be 10 $\mu_B/T$, a typical value for the divalent Cu. The spins at this dimer-like site may give a crucial effect to the anomalous magnetism in this material.

Finally, a complete assignment of observed specific peaks in groups II-IV to the three Cu sites requires separation of the two contributions from hyperfine field and EFG to the shift. This can be done by tracing the detailed angular dependence of the peak shift, and is in progress.

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