NMR study on field-induced charge anomaly in Cu$_3$Mo$_2$O$_9$

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Abstract. A quasi-one-dimensional quantum spin antiferromagnet Cu$_3$Mo$_2$O$_9$, which possesses the two spin degrees of freedom, the linear chain site and dimer-like site weakly interacting with one another, has recently been reported by permittivity and ESR to show a charge instability in its magnetically ordered state. In this article, we report the study on NMR and magnetization to show the existence of the field-induced magnetic phase transition accompanied by the charge anomaly at 8 T.

1. Introduction

A non trivial coupling between spins and charges has recently attracted much interest from both the theoretical and experimental viewpoints as an origin of the multiferroics[1,2]. The target material of this report is a quasi one dimensional antiferromagnetic quantum spin system Cu$_3$Mo$_2$O$_9$, consisting of a spin-1/2 linear chain and spin-1/2 dimer-like pair coupling weakly with one another[3-5]. Existence of these two spin degrees of freedom and of the weak frustration effect suggested an unprecedented spin state, on which intensive studies have been made so far. Recently, Okubo and Kuroe have found independently with different techniques of ESR and the permittivity that a charge instability is induced under high field above 8.5 T in the antiferromagnetically ordered state[6,7]. The latter also tries to explain this instability from the view point of the scaler chirality in the spins on the tetrahedron formed by the dimer-like pair and the two nearest neighbouring spins on the chain[7-9]. The subject of this paper is to detect microscopically the field-induced anomaly at 8.5 T and to clarify the relation between the charge anomaly and the magnetism.

Before entering the subject we briefly summarize the magnetic and structural properties of this system. The intensive study on magnetization and specific heat by Hamasaki et al.[3] has 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, showing a metamagnetism. An anomalous dependence of the magnetisation as well as $T_N$ on the applied field and on its direction are reported and argued to be originated in the quantum fluctuation and frustration effect[11,12]. The weak coupling between the chain site and the dimer-like sites is clearly demonstrated as an existence of the two discrete dispersions by recent inelastic neutron scattering experiments[4-5]. We have shown by NMR in the previous paper[10] that the chain site and the dimer-like site are observed as separate NMR signals and that the staggered hyperfine field produced
by the chain site is geometrically cancelled at the dimer-like sites. However, investigation of a spin structure under the high field, where the charge anomaly is reported, is still untouched. In this paper, we report our NMR and magnetization measurements under high field in the magnetically-ordered state.

2. Experimental
A single crystal with an approximate size of 2 × 4 × 10 mm³ was prepared by an infrared imaging furnace [4, 5]. ⁶³/⁶⁵Cu-NMR experiments were performed in a temperature region 3.7-40 K by a conventional spin-echo method using a 20 T superconducting magnet at HFLSM at IMR, Tohoku Univ. Spectra are measured in the field region 0-16 T directed along c or a-axis. Magnetization curves were measured in the field and temperature region of 0-9 T and 4-7 K by PPMS produced by Quantum Design Co. Ltd. The space group of the compound is Pnma. Schematics of crystal structure and exchange bonds are shown in Fig. 1. There are three 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 the glide symmetry in a unit cell[3]. The two antiferromagnetic interactions J₃ in the chain and J₄ in the dimer are dominant, while the chain-dimer interactions J₁ and J₂ are very weak[3-5]. However the effect of J₁ and J₂ cannot be neglected, because they are responsible for the coupling between the chain and the dimer-like sites.

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. The principal axis of each pair of Cu sites connected with the glide symmetry is oriented symmetrically around crystal axes, so that these glide-pairs are expected to give an identical NMR lines as long as the magnetic field is applied along one of the crystal axes. Figure 2 (a) shows the profile of field-swept

![Figure 1](image1.png)

![Figure 2](image2.png)
3. Results and Discussion

Figure 3 shows the typical spectral profile taken with different resonance frequencies in the magnetically ordered state. We observed six sets of peaks labelled as I, II', II-V. The denotation of the peak groups follows ref. [10], where II' and V were not observed. The spectra measured with various direction of the applied field. One can see that the signal peaks from α and β Cu site degenerate when the field direction is precisely on the c-axis. This alignment reduces the peak number and hence facilitates the peak analysis.

The temperature dependence of the spectral profile of IV is shown in Fig. 2(b), which clearly demonstrates the antiferromagnetic order at \( T_N = 7.9\text{K} \), around which a prominent broadening is observed due to the critical slowing down associated with the second order phase transition. One also notes the complete cancellation of the staggered field produced by the chain at the dimer-like site Cu2 or Cu3 as seen from the fact that no antiferromagnetic splitting is observed below \( T_N \) [10].

Next, we proceed to the anomaly in the higher field region above 8 T, where, as can be seen in Fig. 3, the peaks in group of V start to split. Each peak in the group V splits into three peaks; only the splitting in the peak of the lower field side is shown in Fig. 3. The peak at the low-field side indicated by a solid line is the inheritance of the original peak, and the other two peaks #A and #B, indicated by an open and a solid arrows newly appear. With raising the magnetic field, the two new peaks shift...
rapidly to the higher field while the original keeps the linearity of $v^0 \gamma$. We plot in Fig. 4 $\Delta H$, the splitting width between #A, #B and the original peak. The $\Delta H$ for #A and #B start to increase at around $H_C (4K) \approx 7.8$ T nearly linearly with $H$ with the same gradient. A measurement above 10 T shows that $\Delta H$ still increases with $H$ in the high field above 11.5 T, where the gradient still keeps constant in an experimental precision $\pm 5 \%$. Generally, the NMR peak splitting is caused by change in the hyperfine field or in the electric field gradient. The appearance of the new peaks indicate that either of the two must becomes inhomogeneous in $H>H_C$, and that this inhomogenisation proceeds with increasing $H$.

In order to discriminate the cause of the splitting, we compare the NMR results with the uniform magnetization curve shown in Fig. 4 (b), where one can see a jump at around 8 T. The field-width of the jump is approximately 0.18 T, shown as an error bar in Fig. 4 (a), is temperature independent. The transition field $H_{SF}$ is defined as the midpoint of the jump. An appreciable hysteresis is observed within the jump region, indicating that this phase transition is of 1$^\text{st}$ order. The hysteresis is observed also in the field-swept NMR spectra in the vicinity of $H_C$. The amount of the magnetization jump at $H_{SF}$ is roughly a half of that at 1 T [3]. As shown in Fig. 4 (a), $H_{SF}$ increases with temperature and tends to coincide with the phase boundary of $T_N$, forming a tricritical point[7].

The field position of the magnetization jump $H_{SF}$ coincides with that of the permittivity anomaly [7] and also with $H_C$, where NMR peak-split starts, indicating the close relation between the charge anomaly and the magnetism. Since the NMR splitting width $\Delta H$ continues to increase with increasing $H$ even after the magnetization jump, we can conclude that the origin of the NMR splitting is the inhomogenisation in $v^0_\gamma$ rather than that in the hyperfine field. Here we can depict the relation between the phenomena as following. First, the change in the spin structure at $H_{SF}$ act as trigger and observed as a magnetization jump. The spin structure above $H_C$ may cause the charge anomaly such as the charge disproportionation, possibly by a mechanism proposed in ref. [7], and the latter is observed as the NMR peak splitting.

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