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 as an origin of the multiferroics from both the theoretical and experimental viewpoints[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 viewpoint of the scalar chirality in the spins on the tetrahedron formed by the dimer-like pair and the two nearest neighboring 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 metamagnetization 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 antiferromagnetic staggered moment...
is dominated by the chain site and 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]. $^{63/65}$Cu-NMR experiments were performed in a temperature region 5-40 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 $\alpha$ and $\beta$ connected with the glide symmetry in a unit cell[3]. 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[3-5]. However the effect of $J_1$ and $J_2$ 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. Location of the three Cu sites on the chain and the dimer-like site with dominant exchange interactions (left). Projected view on $ac$ plane, with principal axes of electric field gradient tensor (right).

Figure 2. Peak profiles of the dimer-like site measured (a) with various field directions near $H//c$-axis, and (b) at various temperatures above and below $T_N$. 
3. Results and Discussion

Figure 3 shows the typical spectral profile 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 are not observed. The peaks belonging to group I correspond to Cu1 site and appear at the lower field region outside of Fig. 3. All the other peaks in II’ and II-V come from the dimer-like site. One can clearly see that all the peaks in II’ and II-IV shift linearly to higher field as $\omega/\gamma+C$ with increasing resonance frequency $\omega$ as long as the applied field is below 9 T, where $\gamma$ is the gyromagnetic ratio of $^{63,65}$Cu or $^{65}$Cu, and $C$ is the constant. This good linearity indicates that the hyperfine fields at Cu2 and Cu3 are independent of the applied field. There observed no other peaks in higher fields up to 16 T, indicating that all the eqq-split peaks of Cu2 and Cu3 belong to one of the II’ and II-IV groups and hence that some resonance lines must accidentally overlap with one another to form a single peak. It can also be deduced that the uniform moment at the Cu2 and Cu3 must differ appreciably, from which the site derives its name dimer-like site.

The temperature dependence of the spectral profile of IV is shown in Fig. 2(b), which clearly demonstrates the antiferromagnetic order at $T_N=7.9\text{K}$, where the prominent broadening is observed due to the critical slowing down associated with the second order phase transition. It also demonstrates 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 $T_N$.

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 lowest field indicated by a solid line is the inheritance of the original peak, and 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 $\omega/\gamma$. We plot the splitting width $\Delta H$ between
each two peak and the original one in Fig. 4. They start to increase at around $H_C(4K) \approx 7.8$ T nearly linearly with $H$ with the same gradient. A tentative measurement above 10 T shows that $\Delta H$ still increases with $H$ in the high field above 11.5 T, though the gradient decreases. 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 the 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$^{st}$ order. 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].

This behaviour of magnetization coincides with the results of permittivity [7] and also NMR, 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 $v_0$ rather than that in the hyperfine field. Here we propose a model that the change in the spin structure act as trigger, causing 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. From the splitting width $\Delta H/63\gamma \approx 1 \text{ MHz}$ observed at around $H=10$ T , we can make a tentative estimation for the amount of charge segregation. For the $\Delta H/63\gamma$ is a measure for the change in the $v_0$, which is roughly proportional to the local charge concentration, the observed result indicates the 3 or 5 % change of the local charge density at Cu site, which is quite possible value for the charge instability phenomenon.

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References

[1] Kimura T, Goto T, Shintani H, Ishizawa K, Arima T and Tokura Y 2003 Nature 426 55.
[2] Cheong S-W and Mostovoy M, 2007 Nature Materials 6 13.
[3] T. Hamasaki, T. Ide, H. Kuroe, T. Sekine, M. Hase, I. Tsukada, T. Sakakibara, Phys. Rev. B 77, 134419 (2008).
[4] H. Kuroe, T. Hamasaki, T. Sekine, M. Hase, K. Oka, T. Ito, H. Eisaki, and M Matsuda, J. of Phys.: Conf. Ser. 200 (2010) 022028.
[5] H. Kuroe, T. Hamasaki, T. Sekine, M. Hase, K. Oka, T. Ito, H. Eisaki, K. Kaneko, N. Metoki, M. Matsuda, K. Kakurai, Phys. Rev. B 83, 184423 (2011).
[6] S. Okubo, T. Yoshida, M. Fujisawa, T. Sakurai, H. Ohta, T. Hamasaki, H. Kuroe, T. Sekine, M. Hase, K. Oka, T. Ito, H. Eisaki, J. Low Temp. Phys. (2010) 159, 32.
[7] H. Kuroe, T. Hosaka, S. Hachiura, T. Sekine, M. Hase, K. Oka, T. Ito, H. Eisaki, M. Fujisawa, S. Okubo, H. Ohta, arXiv:1106.4077, J. Phys. Soc. Jpn. in press.
[8] Bulaevskii L N, Batista C D, Mostovoy M V, Khomskii D I 2008 Phys. Rev. B78 024402.
[9] Khomskii D I 2010 J. Phys. Condens. Matter 22 164209
[10] Doi K, Hamasaki T, Kuroe H, T. Sekine and T. Goto, J. of Phys.: Conf. Ser. 200 (2010) 022006
[11] Hamasaki T, Kuroe H, Sekine T, Hase M, Kitazawa H 2009 J. Phys. Conf. Series 150 042047.
[12] Hamasaki T, Kuroe H, Sekine T, Akaki M, Kuwaha H and Hase M, J. Phys. Conf. Ser. 200 (2010) 022013.