Spin lattice relaxation of proton NMR in Mn formate di-urea single crystal at low temperatures

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Abstract. We have studied the spin-lattice relaxation of proton-NMR on the antiferromagnetic Mn formate di-urea below the Néel temperature. Two kinds of relaxation time, $T_1'$ and $T_1''$ are observed. When temperature decreases, $T_1'$ increases slightly and $T_1''$ shows a minimum. This suggests that two kinds of temperature dependence of Mn$^{2+}$ spontaneous magnetizations coexist.

1. Introduction

In connection with the order-disorder problem of Heisenberg antiferromagnets on the 2-D lattice, a crystal of Mn(HCOO)$_2$∙2H$_2$O (hereafter Mn2H) has been interested [1]. Below Néel temperature ($T_N = 3.78$ K), there are two different layers, A and B. The spins take an ordered state only in the layer A, and the B is still with a paramagnetic state [2].

In our experiments, Mn(HCOO)$_2$ ∙2(NH$_2$)$_2$CO (hereafter Mn2U) is used, which is a compound derived from Mn2H by replacing the water molecules by 2(NH$_2$)$_2$CO [3]. The crystal structure of Mn2U is similar to that of Mn2H [4]. However, the heat capacity measurement shows a little difference between Mn2H and Mn2U: Below $T_N$ (at $T / T_N = 0.46$), the Mn ions in Mn2H show a Schottky-type heat capacity under the weak exchange field from the ordered Mn ions in the layer A, and the spin-axis is reoriented [5]. Takeda et al. [5] show that the Mn2U does not contain the paramagnetic state of the layer B ions as in Mn2H, and conjectured that the magnetic structure of Mn2U takes an ordered state only in the layer A. The Mn2U belongs to a frustrated system. The antiferromagnetic exchange interaction between neighboring ions forming the lattice in the layer A is very strong, and in the layer B, the exchange interaction is quite weak, while the interaction between ions belonging to different layers is also weak as same as Mn2H ($J_{AA} = 0.35$ K, $J_{AB} = 0.025$ K [6]).

On the magnetic material, the spin-lattice relaxation time $T_1$ of NMR is used for studying the fluctuation of $S_z$, the $z$-component of electron spin [7]. That is, $1/T_1 \propto \int < \delta S_z (0) \delta S_z (t) > \exp(i\omega t) dt$, where $\delta S_z = < S_z > - S_z$, $< >$ denotes thermal average of the spin correlation function on time $t$ and $\omega$ is a NMR frequency [7]. In the ordered state, $T_1$ increases generally as the temperature decreases. On the other hand, as the temperature approaches to the transition temperature, the $T_1$ decreases because of the large fluctuation of spins.

In our experiment, two kinds of spin-lattice relaxation time $T_1'$ and $T_1''$ are observed. Below the Néel temperature, as the temperature decreases, $T_1'$ slightly increases and the $T_1''$ shows a minimum.
This result suggests that two kinds of temperature dependence of Mn$^{2+}$ spontaneous magnetizations coexist in the temperature range 3.78 K down to about 2.2 K.

2. Experimental results and discussion

We have studied $T_1$ of proton NMR with a conventional pulsed NMR apparatus. The observed NMR frequencies are from about 8 to 20 MHz. The sample Mn2U (here, the 2(NH$_2$)$_2$CO is replaced by 2(ND$_2$)$_2$CO), which is designed, compounded, and crystallized by Yamagata et al.[3], is immersed in a Dewar vessel filled with liquid helium. The temperature is determined from the saturated vapor pressure of helium. The pressure is held constant with a pressure controller having a thin rubber sheet. The temperature is ranged from 1.2 to 4.2 K.

The $T_1$ is measured with the following method: at the time $t_w = 0$, a comb pulse (8 rf-pulses) is applied to the sample. By the comb pulse, the spin echo signal is almost erased. After a time $t_w > 0$, the intensity of spin echo signal is measured as a function of $t_w$. 20 echo signals are collected in this way to have a better signal-to-noise ratio.

Figure 1. The spin-echo intensity $\ln(I_0 - I)$ gives a function of $t_w$. The measurement frequency is 20.6 MHz, and the magnetic field applied to the $c$-axis. (a) shows the data at 2.2 K with 0.5161 T, and (b) gives the data at 3.0 K with 0.4206 T.

Figure 1 shows the spin-echo intensity $\ln(I_0 - I)$ as a function of $t_w$ in the different temperatures, where $I_0$ and $I$ are the spin echo intensity without and with a comb pulses. In Fig. 1(a), at 2.2 K, the experimental result shows only one spin-lattice relaxation time, the inclination gives $T_1 = 1.6 \pm 0.1$ ms. And, in Fig. 1(b), there are two spin-lattice relaxation times, $T_1'$ and $T_1''$ are observed, at 3.0 K, the inclinations give the $T_1' = 1.9 \pm 0.1$ ms, and the $T_1'' = 11.8 \pm 0.1$ ms.

Figure 2 gives the temperature dependence of $T_1'$ and $T_1''$ below the antiferromagnetic phase transition temperature. The temperature dependence of $T_1'$ shows the typical behavior of a magnetic compound in the ordered state. On the other hand, $T_1''$ shows a minimum around $T = 2.2$ K. Below 2.2 K, $T_1''$ is almost equal to $T_1'$, which means the Mn$^{2+}$ spins in layer B are almost in the same ordered state as those in the layer A. This suggests that Mn spins in the layer B show the ordered state at lower temperature than those in the layer A.

As mentioned above, the heat capacity measurement of Mn2U doesn’t show a Schottky-type heat capacity [5]. However, comparing the data of Fe2H, a small bulge is found below the Néel temperature. That is, the result of the heat capacity measurement also shows anomaly below Néel temperature.
In conclusion, due to the frustration, our NMR experiments suggest there are two states in Mn2U below Néel temperature, one is the antiferromagnetic ordered state in the layer A, and another is an unknown state in the layer B. However, around 2.2 K, the Mn spins of the layer B take the same ordered state as those in the layer A. To certify the phase transition and determine the magnetic structure, specific heat and neutron diffraction experiments are needed in progress.

The authors wish to express their gratitude to Dr. K. Okada for his help in experiments and in preparation of this paper.

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