NMR Study of Formate Dihydrate at Millikelvin Temperatures

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Abstract

We have observed the ^{59}Co spin echo signal in $\mathrm{Co(HCOO)_2{\cdot}2H_2O}$ by pulsed NMR below 200mK down to 40mK using a dilution refrigerator. A series of $\mathrm{M(HCOO)_2{\cdot}2H_2O}$ (M = Co and Cu) have a magnetic sandwich structure in which one plane is ferro- or antiferromagnetic while another plane remains paramagnetic. Below the transition temperature we have studied the temperature dependence of the spontaneous sublattice magnetization in both planes by measurement of ^{59}Co NMR spectra.

Key words: NMR; millikelvin temperatures; formate dihydrate; spontaneous magnetization

We have investigated a series of $\mathrm{M(HCOO)_2{\cdot}2H_2O}$ where M stands for Co and Cu. The crystal structure belongs to the monoclinic group $\mathrm{P2_{1/c}}$ and all $\mathrm{M^{2+}}$ ions are surrounded by six oxygen atoms with octahedral coordination. These salts have two kinds of magnetic ion $\mathrm{M^{2+}}$ which show different magnetic characters. Therefore they have two sublattices in a unit cell. The crystal structure of these salts is shown in figure 1. $\mathrm{M^{2+}}$ ions on (100) plane (hereafter A-ions) are coupled with each other by four COOH bonds which mainly contributed to superexchange intraplane interaction between A-ions J_{AA}. On the other hand, $\mathrm{M^{2+}}$ ions on (200) plane (hereafter B-ions) are coupled to A-ions on the adjacent A-planes by a COOH bond. Therefore, the interplane interaction J_{AB} is very small compared to J_{AA}. The intraplane interaction between B-ions via two water molecules can be neglected. Below transition temperature the A-plane set into the magnetic ordered state, while the B-plane remains paramagnetic state. As a result, these substances have a sandwich structure. The paramagnetic plane is sandwiched by the magnetic ordered planes.

The dilution refrigerator has been built in order to carry out NMR measurement in a millikelvin temperature region.[1] The mixing chamber and sample cell are made of STYCAST-1266 to prevent an eddy-current heating by RF pulse. The demountable seal with soap and glycerine is used to connect the sample cell to the mixing chamber. With this seal it is easy to exchange the samples which are immersed in the superfluid phase of the ^{3}He-^{4}He mixture. We have studied the temperature dependence of the NMR spectrum using this dilution refrigerator. The spin-spin relaxation time T_2 is also measured. The NMR frequency range is from 150MHz up to 300MHz. The temperature range is from 1K down to 40 mK. We have observed the ^{59}Co spin echo signals on $\mathrm{Co(HCOO)_2{\cdot}2H_2O}$.

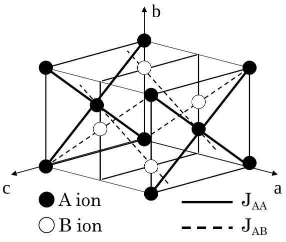

Fig. 1. A schematic drawing of the crystal structure of $\mathrm{M(HCOO)_2{\cdot}2H_2O}$ in which J_{AA} is COOH bond on A-plane and J_{AB} is COOH bond between A- and B-planes.

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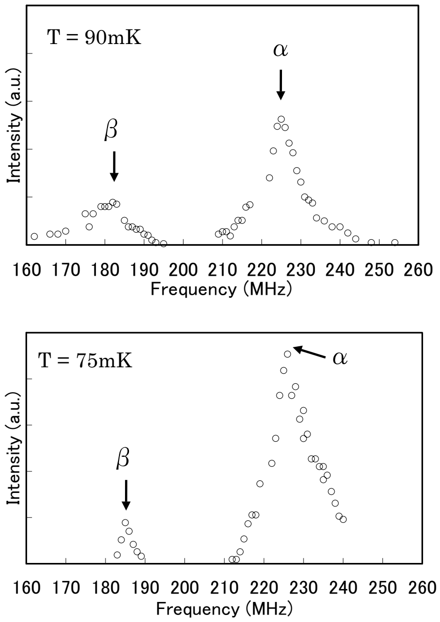

Fig. 2. The ^{59}Co NMR spectra of $Co(HCOO)_2 \cdot 2H_2O$

This substance has been studied by various experimental methods. From these results on this substance A-plane shows a canted antiferromagnetic order but B-plane remains paramagnetic below T_N(5.1K).[2] The heat capacity of this substance shows a peak associated with the phase transition at T_N and Schottky-like anomaly around 0.5K. Therefore, far below 0.5K the B-planes are expected to be in a long range order. It is also expected that the ^{59}Co spin echo signal is observed about 200MHz[2] by our calculations. Although far below T_N the spontaneous sublattice magnetization in A-planes (hereafter M_A) is almost saturated the spontaneous sublattice magnetization in B-planes (hereafter M_B) is not saturated.[3] Therefore, M_A is larger than M_B. M_B increase as the temperature decreases, while M_A is almost independent of temperature. The ^{59}Co NMR frequency ν_n is expressed as $\nu_n = A\langle S\rangle/h$, where A is the hyperfine coupling constant, $\langle S\rangle$ is the thermal average of electron spin in Co^{2+} and h is Plank's constant.

Figure 2 shows the observed ^{59}Co NMR spectra of Co(HCOO)$_2$·2H$_2$O at 90mK and 75mK without external magnetic field . As shown in figure 2, α and β stands for the peaks of the resonance frequencies, α-signal denotes higher frequency one and β-signal denotes lower frequency. The α-signal has been observed below 200mK, in which the β-signal has been observed below 100mK. T_2 of α-signal is 1μsec at 90mK, while T_2 of β-signal is much shorter. The α-signal intensity is stronger than β-signal. From these results the fluctuation of hyperfine field at the nucleus on β-signal is large. As shown in figure 2, the NMR frequency of α-signal is higher than that of β-signal. From this result the spontaneous sublattice magnetization of α-signal is larger than that of β-signal. The NMR frequency of α- and β-signal increase as the temperature decreases. This shows the temperature dependence of the spontaneous sublattice magnetization of α-signal is larger than that of β-signal.

In conclusion, we has been observed the ^{59}Co NMR signals for the first time in millikelvin temperature region using a dilution refrigerator. The α-signal corresponds to the ^{59}Co NMR frequency in A-planes and the β-signal corresponds to the ^{59}Co NMR frequency in B-planes. From the observation of the ^{59}Co NMR frequency we have observed selectively each spontaneous sublattice magnetization in this substances. The ratio of the spontaneous sublattice magnetization M$_B$/M$_A$ is about 0.81 at 90mK and 0.82 at 75mK.

References

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