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Effect of pressure on two-dimensional Heisenberg antiferromagnet $Cu(HCOO)_2 \cdot 4H_2O$

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Abstract

The effect of pressure on two-dimensional Heisenberg antiferromagnet $Cu(HCOO)_2 \cdot 4H_2O$ has been investigated through X-ray diffraction, susceptibility and magnetization curve measurements. The pressurization induces the paramagnetic behavior above 1.4 kbar. The paramagnetic component increases continuously with increasing pressure, and the antiferromagnetic ordering and field-induced phase transition vanish above 2.8 kbar. The X-ray diffraction pattern at 6.6 kbar is not that of $Cu(HCOO)_2 \cdot 4H_2O$ but $Cu(HCOO)_2 \cdot 2H_2O$. Therefore, the pressurization induces the crystal structural change from $Cu(HCOO)_2 \cdot 4H_2O$ to $Cu(HCOO)_2 \cdot 2H_2O$ with dehydration.

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1. Introduction

Since the magnetic property and the crystal- and magnetic-structure are closely related with each other, the change in crystal structure by pressurization is supposed to induce the magnetic phase transition. Copper formate tetrahydrate Cu(HCOO)₂·4H₂O (abbreviated as CFT) [1–3] is a nearly two-dimensional S = 1/2 Heisenberg antiferromagnet. The crystal structure is characterized by alternately stacked copper formate and H₂O planes along the *c*-axis. Copper ions linked by HCOO⁻ group form the two-dimensional network parallel to the a-b plane. The antiferromagnetic order is observed below $T_{\rm N} = 17$ K. The magnetic interaction of intralayer is estimated to be about 36 K, and there is weak coupling $(10^{-1}-10^{-3})$ between neighboring copper fomate layers [3]. The field-induced weak ferromagnetism accompanies the field-induced change of the magnetic structure from four- to two-

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sublattice state at $H_c = 4 \text{ kOe}$. It is interesting to study the modification of magnetic structure and phase transition through control of the dimensionality by pressurization. We investigated the effect of pressure on CFT through X-ray diffraction, susceptibility and magnetization measurements.

2. Experimental

The single crystals of CFT were grown by slow cooling an aqueous solution from about 40 °C at a rate of 1 °C/day [4]. The DC susceptibility and magnetization measurements of the single crystal and powder samples were calculated using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). The hydrostatic pressure was attained using a pistoncylinder type pressure cell. The X-ray diffraction measurements of the powder samples with a diamond anvil cell at room temperature under pressure were carried out using a synchrotron-radiation X-ray diffractometer at beam line

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1B of the Photon Factory (in KEK, Japan) operated at a wavelength of 0.6876 Å calibrated with CeO₂ powder diffraction pattern.

3. Results and discussion

Fig. 1 shows the pressure dependence of susceptibility of the CFT single crystal for the field H = 0.1 kOe applied along the b axis, which is smaller than critical field of the field-induced phase transition. The susceptibility at ambient pressure shows the peak corresponding to the antiferromagnetic ordering at $T_{\rm N} = 17$ K. Below 1.4 kbar, the susceptibility is similar to that at ambient pressure, while the paramagnetic behavior suddenly appears above 1.4 kbar. The paramagnetic component increases continuously with increasing pressure, and the antiferromagnetic order vanishes above 2.8 kbar. The magnetic ordering temperature does not depend on pressure below 2.8 kbar. Fig. 2 shows the pressure dependence of magnetization curve of CFT of single crystal at 5K for the filed applied along the *b*-axis. The magnetization curve at ambient pressure has a jump at $H_c = 4$ kOe due to the field-induced phase transition. The magnetization curve below 1.4 kbar is similar to that at ambient pressure; however, the paramagnetic component is induced above 1.4 kbar. The jump of magnetization curve disappear above 2.8 kbar. The critical field does not depend on pressure below 2.8 kbar. After depressurization, the susceptibility and the magnetization curve does not return to those before pressurization, however, the antiferromagnetic order reappeared at same temperature.

We analyzed the results for susceptibility $\chi(P)$ and magnetization M(P) under pressure as the summation of the antiferromagnetic component of CFT and the



Fig. 1. The pressure dependence of susceptibility of the CFT single crystal. The solid lines are the calculated value (see text). The inset shows the pressure dependence of α (\bigcirc) and β (\Box) determined using $\chi(P)$ and M(P), respectively.



Fig. 2. The pressure dependence of magnetization curve of the CFT single crystal at 5 K. The solid lines are the calculated value (see text).

paramagnetic one with the Curie–Weiss law and Brillouin function B_S :

$$\chi(P) = \alpha \chi(P = 0 \text{ kbar}) + (1 - \alpha) \frac{C}{T - \Theta},$$
$$M(P) = \beta M(P = 0 \text{ kbar}) + (1 - \beta) Ng \mu_{\text{B}} SB_{S} \left(\frac{g \mu_{\text{B}} H}{k_{\text{B}} T}\right),$$

where α and β are the amount of spin of the antiferromagnetic components of CFT and the quantity $(1-\alpha)$ and $(1-\beta)$ correspond to the amount of the induced S = 1/2paramagnetic one. As shown in Figs. 1 and 2, the experimental results under pressure are well reproduced using $\chi(P)$ and M(P) with the values of α and β shown in the inset of Fig. 1. The two values begin to decrease at 1.4 kbar and are reduced to zero above 2.8 kbar. In the case of powder samples, we obtained similar results with those of the single crystal.

We performed X-ray diffraction measurements under pressure to investigate the origin of the pressure-induced paramagnetic behavior. The diffraction pattern at 6.6 kbar changes from that of ambient pressure and is the similar profile to copper formate dihydrate $Cu(HCOO)_2 \cdot 2H_2O$ (abbreviated as CFD). The results indicate that the crystal structure changes from CFT to CFD by pressurization. The diffraction pattern after releasing the pressure contained both CFD profile and CFT one, which indicate that depressurization induced recrystallization of CFT partially.

CFD is a ferromagnetic compound with the Curie temperature $T_{\rm C} = 0.75$ K [5] and exhibits paramagnetic behavior in the present experimental region. Therefore, the experimental results suggest that the pressure-induced paramagnetic component is attributed to the paramagnetic behavior of CFD and CFD coexists with CFT between 1.4 and 2.8 kbar. The pressure dependence of α and β shows that the fraction of CFD increases continuously between 1.4 and 2.8 kbar, and above 2.8 kbar the system changes to that of CFD in both the magnetic properties and the crystal structure.

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