Two-dimensional $S = 1$ spin-gap antiferromagnet m-MPYNN$\cdot$ BF_4 in magnetic fields

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Abstract

We have measured the magnetic susceptibility, χ, the magnetization, M, and the heat capacity, C, of m-MPYNN$\cdot BF_4$ which is an organic spin-1 *Kagomé* antiferromagnet with an isotropic g-factor, in magnetic fields. A non-magnetic ground state was indicated by a steep decrease of χ below 0.25 K or 0.4 K in zero field. The sample dependence of χ observed below about 3 K is probably due to defects of the crystal. We have found that M/H is not affected by the field up to 10 mT. The temperature dependence of C observed had two maximum. The maximum at $T = 1.6$ K in zero field changes with the field, reflecting the competition between the antiferromagnetic interaction and the Zeeman energy. Another maximum at 0.12 K does not change up to 4 T, which shows that the peak is not related to the spin entropy.

Key words: spin-gap; Kagomé antiferromagnet; magnetic frustration

1. Introduction

m-MPYNN$\cdot$X$\cdot$(1/3)(acetone) (X = BF_4, ClO_4, I) is a unique system of the two-dimensional (2D) *Kagomé* $S = 1$ antiferromagnet of which ground state is of considerable interest from the viewpoint of the spin frustration. In this organic material, the organic radical cation m-MPYNN$^+$ which have a spin 1/2 with an isotropic g-factor of 2.006 crystallizes in a 2D layer. Two radical spins on each side of the triangular lattice form a spin 1 dimer coupled through a strong ferromagnetic interaction $2J_0$, and the ferromagnetic dimers form the *Kagomé* lattice connected by an antiferromagnetic interaction $2J$[1]. Recent measurements of heat capacity and magnetic susceptibility of m-MPYNN$\cdot BF_4$ in zero field have revealed that a non-magnetic 2D spin-gap state exists at low temperatures and that the spin gap energy is about 0.25 K. The spin-gap state have been confirmed also in the μSR experiment [3], and studied theoretically on the state at $T = 0$ [4], although, the detailed picture is still unknown.

In this article, we have studied the magnetic susceptibility, the magnetization, the heat capacity of m-MPYNN$\cdot BF_4$, applying magnetic fields to study the field dependence of the spin-gap state.

2. Results and discussion

The ac susceptibility, χ, and the magnetization, M, have been measured by an SQUID magnetometer between 80 mK and 7 K. All measurements including heat capacity were carried out on crystal samples, which were newly synthesized by the same method as that of Ref. [2]. In addition, more care was taken to avoid the evaporation of the solvent from the crystal.

In Ref. [2], we have reported that χ of this material collapse to almost zero below 0.2 K, which indicates the

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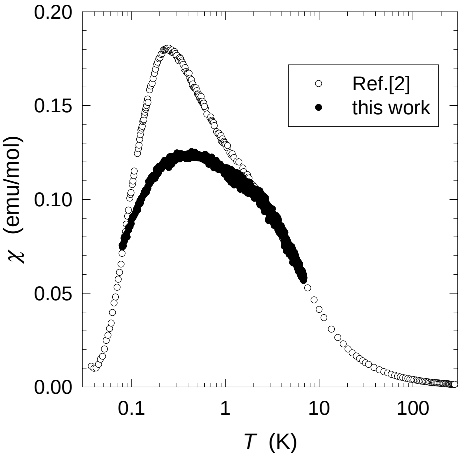

Fig. 1. Susceptibilities of some m-MPYNN·BF_4 samples. The higher-peak curve was measured in Ref. [2]. The other curve was done in this work. In both measurements, χ 's decrease to be almost zero at the low temperatures, which indicates the existence of the spin-gap state.

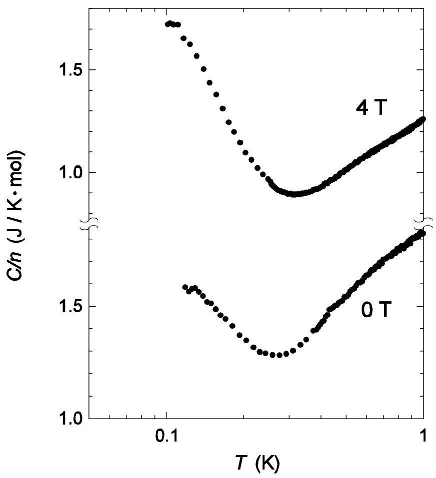

Fig. 2. Temperature dependences of the heat capacity in zero field and 4 T. The curves have been offset for clarity.

existence of a nonmagnetic spin-gap state. The similar behavior has been observed in the present sample. In Fig. 1, the zero-field temperature dependence of χ are shown together with previous data in Ref. [2]. Above 3 K, both samples have the same temperature dependence of χ, which indicates that the magnitudes of interactions J and J_0 of the present sample are the same as the previous ones. Besides, the temperature dependences of C of both samples are the same, as we mention later. They suggest that both samples have the same basic property. On the other hand, a difference of χ appears below 3 K. The present sample shows a rather broad peak at $T_0 = 0.45$ K, comparing with a sharp peak at $T_0 = 0.24$ K of the previous sample. This difference is attributed to the sample dependence, and suggests that the present sample has a larger spin-gap energy, since T_0 corresponds to the spin-gap energy, Δ, assuming the form $\chi \propto A/T \exp(-\Delta/T)$. In addition, the temperature hysteresis below T_0 seen in the previous sample is absent in the present sample. They imply that the present sample has less defects due to the evaporation of the solvent than the previous one.

We have also measured magnetizations applying fields of 2 and 10 mT. Observed M/H 's are the same in both fields, and also as the ac susceptibility. Results suggest that $k_B\Delta$ is much larger than the Zeeman energy $\mu_B H$ in 10 mT ($\sim$ 7 mK).

To see the other macroscopic property in fields, we have measured heat capacities in several fields up to 4 T. Heat capacities, C, have been measured using by the usual adiabatic heat pulse method. C had two maximums, one is at $T_1 = 1.6$ K, which is about a half of the antiferromagnetic interaction $2J/k_B = 3.1$ K, and the other is at about $T_2 = 0.12$ K. It is the same as that of the previous sample in Ref. [2]. C around the peak at T_2 in zero field and 4 T are plotted in Fig. 2. The peak has continued to exist in high magnetic fields up to 4 T, and T_2 has not changed. The difference of heights of the peak is attributed to the background by the envelope of another peak at T_1. Since the Zeeman energy $\mu_B H$ in 4 T ($\sim$ 2.7 K) is comparable to $2J$ (=3.7 K), we have concluded that the peak at T_2 is not due to magnetism. It agrees with that the excess of entropy have been pointed out in Ref. [2]. To see the contribution of the spin-gap state to C, subtraction of the peak at T_2 is required. On the other hand, The maximum of C observed at T_1 changes with the field, reflecting the competition between the antiferromagnetic interaction and the Zeeman energy. T_1 increased linearly in high fields above 2 T.

We have measured the susceptibility, the magnetization, and the heat capacity of the *Kagomé* $S = 1$ antiferromagnet m-MPYNN·BF_4 in magnetic fields. We found that M/H is not affected by a field up to 10 mT. We clarified that the peak of C at 0.12 K seen in Ref. [2] is not due to the spin entropy.

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