Ferromagnetic ordering of $S=\frac{1}{2}$ Heisenberg ferromagnetic chains in organic magnet β-BBDTA·$GaBr_4$

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We have observed the magnetic susceptibility and the specific heat of the β phase of an organic magnet BBDTA·$GaBr_4$ which consists of antiferromagnetic chains and ferromagnetic chains. At low temperatures, the antiferromagnetic chains do not contribute to the magnetic property because of a large intrachain interaction of −197 K. The ferromagnetic chains show a three-dimensional magnetic ordering at 0.4 K. The low-temperature susceptibility and the specific heat in magnetic fields are quantitatively reproduced by calculations for the $S=\frac{1}{2}$ Heisenberg ferromagnetic chains with $2J_F=8.7$ K interacting only by a ferromagnetic interchain interaction of $2zJ'=0.29$ K. It indicates that this organic magnet realizes a model system of Heisenberg ferromagnets.

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Organic radical magnets have attracted much interest as actual Heisenberg spin systems, where an unpaired electron on a molecular orbital has a spin $S=\frac{1}{2}$ with an isotropic g factor due to the orbital quenching. Exact solutions theoretically calculated for one-dimensional (1D) magnets have been confirmed by experiments for quasi-1D organic magnets. The experimental results and magnetic properties derived from exact solutions have quantitative agreements within the experimental error, where the temperature is sufficiently higher than the interchain interaction.[1] Another interest is a ferromagnet of organic material which is free of the usual magnetic ions such as transition metals. A ferromagnetic interaction results from the orthogonality of the molecular orbitals of the unpaired electron, in contrast to the usual antiferromagnetic bonding. Recently long-range ordering to a ferromagnet was found at 0.6 K in the β phase of p-NPNN.[2] In the case of magnets based on quasi-1D ferromagnets, a positive Curie-Weiss temperature was observed in the γ phase of p-NPNN, but it has a long-range antiferromagnetic ordering of ferromagnetic chains at low temperatures.[3,4] The magnetic susceptibility and the specific heat in magnetic fields quantitatively agree with calculations for $S=\frac{1}{2}$ Heisenberg ferromagnetic chains with both ferromagnetic and antiferromagnetic interchain interactions.[4] Ferromagnets composed of ferromagnetic chains without an antiferromagnetic interchain interaction have not been reported so far.

In this article, we show the finding of a ferromagnet composed of ferromagnetically interacting ferromagnetic chains realized in an organic magnet β-BBDTA·$GaBr_4$. We have determined the low-temperature state of β-BBDTA·$GaBr_4$ by measurements of the magnetic susceptibility and specific heat. A 3D ordering of ferromagnetic chains is observed at 0.4 K in zero field. The ordering temperature shifts higher when a magnetic field is applied, which is an important feature of a ferromagnetic ordering. Furthermore, quantitative agreements of the experimental results with theoretical calculations indicate that, at low temperatures, this organic ferromagnet is completely described as $S=\frac{1}{2}$ Heisenberg ferromagnetic chains where the interchain interaction is purely ferromagnetic without antiferromagnetic interaction.

BBDTA (=benzo[1,2-d:4,5-d']bis[1,3,2]dithiazole)·$GaBr_4$ has three different polymorphs labeled α, β, and γ,[5] which have different magnetic properties from those of BBDTA·$GaCl_4$ with different nonmagnetic counter-anions.[6] In the β phase, β-BBDTA·$GaBr_4$, organic layers of radical cations $BBDTA^+$ with an isotropic spin $\frac{1}{2}$ are separated by nonmagnetic anions $GaBr_4^-$. In each organic layer shown in Fig. 1(a), two kinds of magnetic chains with different arrangements appear alternately, which are referred to as chains I and II, hereafter. Because of the large intermolecular contact between sulfur and nitrogen in chain I, the intrachain interaction in chain I is antiferromagnetic and on the order of 100 K. The magnetization curve at 2 K is shown in Fig. 1(b). The magnetization saturates above around 30 kOe at a half of the total saturation magnetization [=5585 erg/(Oe mol)] of the organic radical spins. No magnetization of chain I is observed reflecting the large antiferromagnetic interaction. Saturation of spins in chain II around

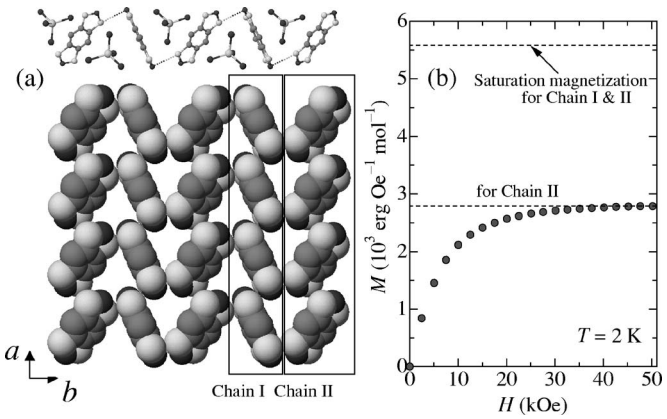

FIG. 1. (a) Organic layer of β-BBDTA·$GaBr_4$ shown in the ball and stick model and the space filling model. $GaBr_4^-$ anions are not indicated in the space filling model. Along the a axis, there are two kinds of magnetic chains. (b) Magnetization curve of β-BBDTA·$GaBr_4$ at 2 K. The magnetization saturates at a half of the total saturation magnetization, indicating saturation of spins in chain II.

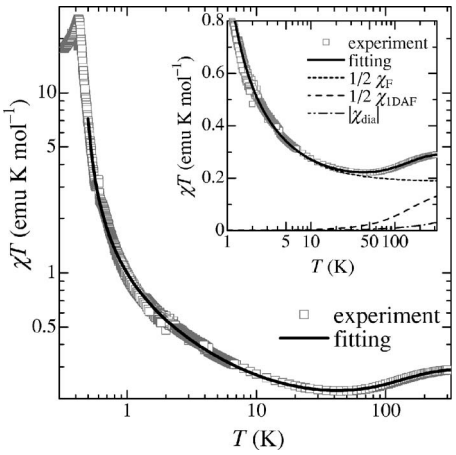

FIG. 2. Magnetic susceptibility of β-BBDTA·$GaBr_4$ plotted as χT. Open squares indicate experimental results. Solid lines are the fitting to a simple sum of susceptibilities for antiferromagnetic chains (chain I) and ferromagnetic chains with ferromagnetic interchain interaction (chain II). The high-temperature region is expanded in the inset. Contributions of each chain are shown by dashed lines. A dot-dashed line indicates magnitude of the diamagnetic susceptibility.

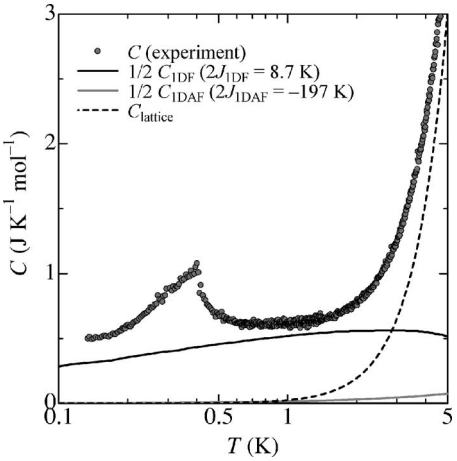

FIG. 3. Specific heat of β-BBDTA·$GaBr_4$ in zero field. A sharp cusp due to the 3D ordering is seen at 0.4 K. Black and gray solid lines indicate exact solutions for the 1D $S=\frac{1}{2}$ Heisenberg ferromagnet (Ref. 8) and the 1D antiferromagnet (Ref. 7) respectively, which are calculated by interactions derived from the susceptibility. The estimated lattice specific heat is shown by dashed line (see text).

30 kOe clearly shows that the intrachain interaction in chain II and the interaction between chains I and II are small.

The magnetic susceptibility χ of β-BBDTA·$GaBr_4$ was measured from 7 K down to 0.3 K by a handmade ac mutual-inductance bridge with a superconducting quantum interference device (SQUID) magnetometer as a null detector. The susceptibility at high temperatures above 2 K was obtained from the magnetization at a field of 10 kOe measured by a commercial SQUID susceptometer (Quantum Design MPMS-XL). The magnitude and offset of the low-temperature data were calibrated against the high-temperature data. χT of β-BBDTA·$GaBr_4$ is plotted in Fig. 2 as a function of temperature T. χT due to chain I with a large antiferromagnetic interaction is observed only above about 40 K. At low temperatures, χT increases rapidly with decreasing T, which indicates a ferromagnetic interaction in chain II. A magnetic ordering is indicated by a maximum in χT at 0.4 K. The magnitude of χ at the maximum ($\sim$61 emu/
mol) is comparable to the saturation value $v/4\pi N_d$ ($\sim$54 emu/mol for a sphere) due to the demagnetizing field, where N_d is the demagnetizing factor and v is the molar volume, indicating that the actual susceptibility diverges at 0.4 K and that the ordering is ferromagnetic.

To analyze the observed susceptibility quantitatively, χ is assumed to be a sum of that from chain I with antiferromagnetic intrachain interaction J_{AF} and that from chain II with ferromagnetic intrachain interaction J_F. Susceptibilities of the $S=\frac{1}{2}$ Heisenberg chain have been exactly calculated.[7,8] For the analysis, we used a fitting[9] $\chi_{1DAF}(J_{AF})$ of the Bonner-Fisher solution for the antiferromagnetic chain[7] and the Padé approximant $\chi_{1DF}(J_F)$ for the ferromagnetic chain.[10] Considering the 3D ordering at 0.4 K, we assumed an interchain interaction J' among the ferromagnetic chain II interaction. Applying the mean-field approximation when the temperature is sufficiently higher than $2zJ'$, the susceptibility of chain II is given by

$$\chi_F(J_F,J') = \frac{\chi_{1DF}(J_F)}{1-\dfrac{2zJ'}{N_A g^2 \mu_B^2}\chi_{1DF}(J_F)}, \tag{1}$$

where z is the number of nearest-neighbor chains II, N_A Avogadro's number, g the g factor of a free electron spin, and μ_B the Bohr magneton. Thus, the experimental data are fitted to the following equation:

$$\chi = \frac{1}{2}\chi_F(J_F,J') + \frac{1}{2}\chi_{1DAF}(J_{AF}) + \chi_{dia}, \tag{2}$$

where χ_{dia} is the diamagnetic susceptibility. As shown by a solid line in Fig. 2, experimental results are well fitted in a wide temperature range from 0.5 K to room temperature, using the fitting parameters $2J_{AF}=-197\pm9$ K, $2J_F=8.7\pm0.7$ K, $2zJ'=0.29\pm0.02$ K, and $\chi_{dia}=-(1.0\pm0.2)\times10^{-4}$ emu/mol. The estimated χ_{dia} is on the order of a value determined by the Pascal law.[11] The inset of Fig. 2 shows the contributions of chains I and II, and χ_{dia}. Below about 20 K—i.e., 1/10 of $|2J_{AF}|$—the susceptibility of the antiferromagnetic chain I is negligible. χ_{dia} is also small in the temperature regime. At low temperatures, the observed susceptibility is $\frac{1}{2}\chi_F$ [Eq. (1)] of $S=\frac{1}{2}$ Heisenberg ferromagnetic chain II with interchain interaction $2zJ'$. It should be noted that, in the case of ferromagnetic ordering, the demagnetizing field works to cancel the molecular field due to $2zJ'$. Thus, the derived value for $2zJ'$ seems to be smaller than the actual interchain interaction by a value on the order of 10 mK.[12]

In the estimation from the susceptibility, we obtained the ferromagnetic interchain interaction $2zJ'$ among the chain II interaction. However, even in the case of p-NPNN[3] where a 3D antiferromagnetic ordering occurs, the interchain interac-

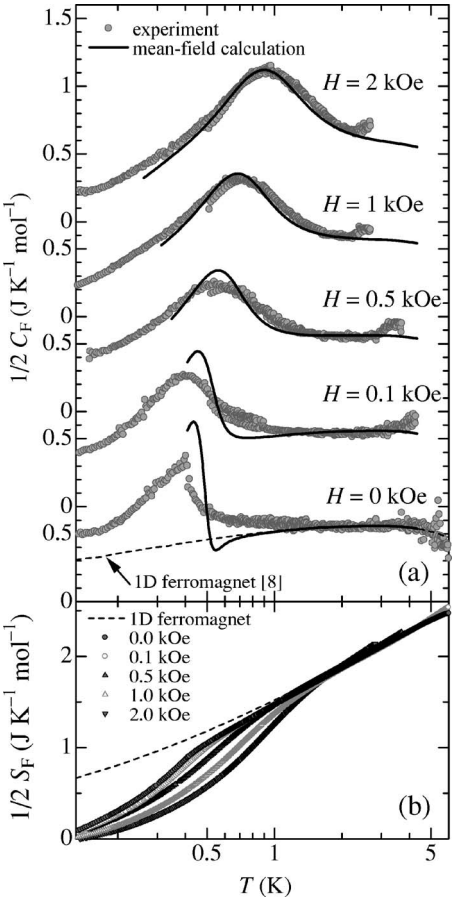

FIG. 4. (a) Specific heat of β-BBDTA·$GaBr_4$ in external fields. The vertical axis is offset for each field. Gray circles are experimental results, and solid lines are calculations for $S=\frac{1}{2}$ Heisenberg ferromagnetic chains with $2J_F$ including the ferromagnetic interchain interaction $2zJ'$ as the mean field. For calculations, interactions derived from the susceptibility, $2J_F=8.7$ K and $2zJ'=0.29$ K, are used. (b) Entropy estimated by integrating the specific heats. Offset of the entropy was adjusted to the exact solution calculated for the 1D $S=\frac{1}{2}$ Heisenberg ferromagnet (Ref. 8) above 2 K.

tion is apparently ferromagnetic on the susceptibility. It is because the actual interchain interaction consists of both ferromagnetic and antiferromagnetic interactions. In order to determine whether the 3D ordering in β-BBDTA·$GaBr_4$ is induced by genuine ferromagnetic interactions, we have measured the specific heat C in magnetic fields up to 2 kOe. The specific heat was measured down to 0.1 K by a hand-made system using the adiabatic heat-pulse method.

The specific heat in zero field is shown in Fig. 3, together with the exact solution for the 1D antiferromagnet,[7] $\frac{1}{2}C_{1DAF}=1/2\times 0.35N_A k_B(k_B T/|J_{AF}|)$, with $2J_{AF}=-197$ K, and that for the 1D $S=1/2$ Heisenberg ferromagnet,[8] $\frac{1}{2}C_{1DF}$, with $2J_F=8.7$ K, using interactions derived from the susceptibility. Around 1 K, the observed specific heat obviously approaches $\frac{1}{2}C_{1DF}$ due to chain II. And then a sharp cusp indicating the 3D transition is observed at 0.4 K, where the magnetic susceptibility shows the maximum. At high temperatures, an upturn due to the lattice specific heat $C_{lattice}$ appears. Assuming the Debye T^3 law, $C_{lattice}$ is estimated to

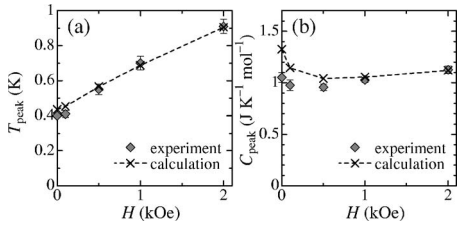

FIG. 5. Field dependence of the specific heat peak due to the 3D ferromagnetic ordering in β-BBDTA·$GaBr_4$. (a) Peak temperature. (b) Peak height.

be $0.0243T^3$ J/(K mol) shown by a dashed line, which is determined so that the C observed above 2 K is a sum of $C_{lattice}$, $\frac{1}{2}C_{1DAF}$, and $\frac{1}{2}C_{1DF}$.

Specific heats $\frac{1}{2}C_F$ of ferromagnetic chain II in various external fields are shown in Fig. 4(a), where $\frac{1}{2}C_{1DAF}$ and $C_{lattice}$ are subtracted from the observed specific heat C. Entropies estimated by integrating C_F/T are shown in Fig. 4(b). The offset of the entropy was adjusted to the exact solution for the 1D Heisenberg ferromagnet[8] above 2 K. Entropies in various external fields tend to become zero at zero temperature, which indicates that the subtraction of $C_{lattice}$ is appropriate. When the external field is applied, the cusp of the specific heat shifts to higher temperature, associated with its broadening even at 0.1 kOe. The rise of the peak temperature T_{peak} with the field is a characteristic of ferromagnets. In terms of the symmetry breaking, the ferromagnetic transition of Heisenberg spins is not defined in an external field. It is indicated by the peak broadening observed in the fields. These properties contrast with those of a sharp peak in magnetic fields, accompanied by an antiferromagnetic ordering of ferromagnetic chains, in γ-p-NPNN.[3]

To evaluate how quantitatively the ferromagnetic ordering of β-BBDTA·$GaBr_4$ is described by theory, we have calculated the specific heat of $S=\frac{1}{2}$ Heisenberg ferromagnetic chains interacting ferromagnetically. We used an exact solution of the $S=\frac{1}{2}$ Heisenberg ferromagnetic chain and the mean-field approximation for the ferromagnetic interchain interaction, in the same way as in Ref. 4. For the calculation, the same parameters obtained from the susceptibility, $2J_F=8.7$ K and $2zJ'=0.29$ K, were used. The calculated specific heat in zero field is shown by a solid line at the bottom of Fig. 4(a) together with that for the 1D ferromagnet without interchain interaction. Above about 2 K, both calculations have the same temperature dependence. The specific heat peak due to the 3D ferromagnetic transition was calculated to be at 0.44 K, close to the experimental $T_{peak}=0.40$ K. The peak height is about 30% higher than the experimental. The difference between the experiment and calculation around the transition temperature is mainly due to 3D fluctuations which are not exactly calculated in the mean-field approximation. In the calculation, another broad maximum due to a 1D short-range ordering is indicated around 3 K. Above about 0.5 kOe, the maximum merges into the peak due to the 3D ordering and becomes a shoulder of the peak.

The observed specific heats at each external field are compared with the calculations in Fig. 4(a). Using no additional adjusting parameters, the calculated specific heat in fields is

quantitatively in good agreement with the experimental results up to 2 kOe.[13] In Fig. 5, the temperature T_{peak} and the height C_{peak} of the specific heat peak due to the 3D ferromagnetic ordering are plotted as a function of the field. Above 0.5 kOe, T_{peak} agrees with the calculation within the experimental error. The C_{peak} in the experiment coincides with the calculation above 1 kOe. In both the experiment and calculation, C_{peak} shows a characteristic minimum around 0.5 kOe. Thus, as well as the susceptibility, the low-temperature specific heat of β-BBDTA·$GaBr_4$ is sufficiently described as an ideal 3D ferromagnetic ordering of $S=\frac{1}{2}$ Heisenberg ferromagnetic chains ($2J_F=8.7$ K) with only ferromagnetic interchain interaction $2zJ'=0.29$ K.

In conclusion, we have studied the magnetic susceptibility and the specific heat of β-BBDTA·$GaBr_4$ composed of two kinds of magnetic chains. One group of chains has a large antiferromagnetic intrachain interaction of $2J_{AF}=-197$ K, so that the magnetic contribution is sufficiently small at low temperatures. We found that the low-temperature magnetism is caused by another group of magnetic chains, where the 3D ferromagnetic transition is observed at 0.4 K. The low-temperature susceptibility and the specific heat in external fields are quantitatively well described by ferromagnetic chains with intrachain interaction $2J_F=8.7$ K and ferromagnetic interchain interaction $2zJ'=0.29$ K without any antiferromagnetic interaction.

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[11] Values in the literature are -1.52×10^{-4} emu/mol for $GaBr_4^-$ and -0.95×10^{-4} emu/mol for BBDTA(neutral) [T. M. Barclay *et al.*, J. Am. Chem. Soc. **119**, 2633 (1997)].

[12] The correction term due to the interchain interaction, $\frac{2zJ'}{N_A g^2 \mu_B^2}$ in Eq. (1), is partly canceled by that due to the demagnetizing field, $-\frac{4\pi N_d}{2v}$. For a sphere, this cancellation corresponds to 14 mK in temperature.

[13] Small deviations from the calculations below about 0.4 K are probably due to the nuclear specific heat of protons proportional to $1/T^2$.