Specific-heat anomaly in the Ising antiferromagnet $FeBr_2$ in external magnetic fields

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Specific-heat measurements have been performed on the Ising antiferromagnet $FeBr_2$ in external magnetic fields. The temperature dependence of the magnetic specific heat shows two anomalies in external fields below the metamagnetic transition field. The anomaly at a higher temperature indicates the phase transition from the paramagnetic to antiferromagnetic phase. The lower-temperature anomaly shows up in the form of a peak superposed on a broad shoulder. The peak becomes sharp with the increase of magnetic field up to 2.9 T, which shows the existence of a new phase under a magnetic field. A theoretical analysis based on the pair approximation and Monte Carlo simulations reproduces the peak at the higher temperature and the broad shoulder. The broad shoulder appears as a result of competition between the nearest-neighbor ferromagnetic and the next-nearest-neighbor antiferromagnetic interactions in the triangular Fe lattice planes. [S0163-1829(96)51638-3]

The layered Ising antiferromagnets FeX_2 (X=Cl, Br, I) have been studied for many years. The compound $FeCl_2$ is a well-known metamagnet in which the magnetization shows a discontinuous change from a state with very small net moment to the saturated paramagnetic state at low temperatures in increasing magnetic field.[1] The compound $FeBr_2$ has the hexagonal CdI_2 structure and becomes antiferromagnetic (AF) below the transition temperature T_N= 14.2 K. The spin arrangement in the ordered state is such that spins in the c plane are parallel with each other and spins between adjacent layers are antiparallel. The easy axis of magnetization is parallel to the c axis. Due to the strong anisotropy, $FeBr_2$ also shows a metamagnetic transition at $\sim$3 T below 4.6 K.[2]

Despite these similarities, $FeBr_2$ behaves differently from $FeCl_2$ in applied magnetic fields.[3–7] From recent experiments[3,4] the existence of a new phase boundary in the temperature T-magnetic field H plane has been suggested. In order to confirm the existence of the new phase boundary, we have performed specific-heat measurements on a single crystal of $FeBr_2$ in applied magnetic fields.

The single crystals of $FeBr_2$ were grown by the Bridgman technique. The specific heat was measured using a MagLab^{HC} microcalorimeter of Oxford Instruments. This calorimeter uses the relaxation method. The single crystal was cut into a platelet parallel to the c plane with the dimensions 4 mm$\times$3 mm$\times$0.5 mm. The platelet was mounted on the sapphire chip using a small amount of grease. Because the crystal is hygroscopic, the sample was handled under dry N_2 gas. The specific heat of the sample was obtained by subtracting the specific heat of the sapphire chip. The sample was usually cooled down to 0.5 K in H and the specific heat was measured on a heating process.

We measured the temperature dependence of the specific heat of $FeBr_2$ in H parallel to the c axis between 0 T and 4 T. In zero field only one sharp peak appears at 14.2 K. This behavior is consistent with the previous report.[8] Typical results measured in finite fields are shown in Fig. 1. Here, we subtracted the contribution of the lattice from the total specific heat using the specific heat of $CdBr_2$,[9] which has the same crystal structure as $FeBr_2$. The result after subtraction corresponds to the magnetic part of specific heat C_{mag} of $FeBr_2$. As shown in Fig. 1, C_{mag} measured in 1.9 T exhibits two peaks located at 12.8 K and 9.8 K. From a careful inspection, we see a broad shoulder around 8 K. We also measured the specific heat under zero-field-cooling condition. The temperature dependence of C_{mag}, however, was not affected by the cooling condition. Therefore, the appearance of two peaks indicates the occurrence of a new kind of phase

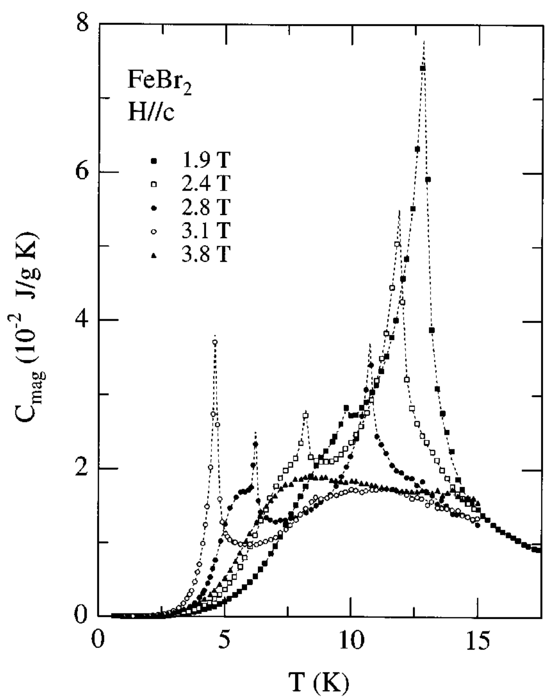

FIG. 1. Temperature dependence of the magnetic specific heat in $FeBr_2$ measured in external fields parallel to the c axis. Dotted lines are guides to the eye.

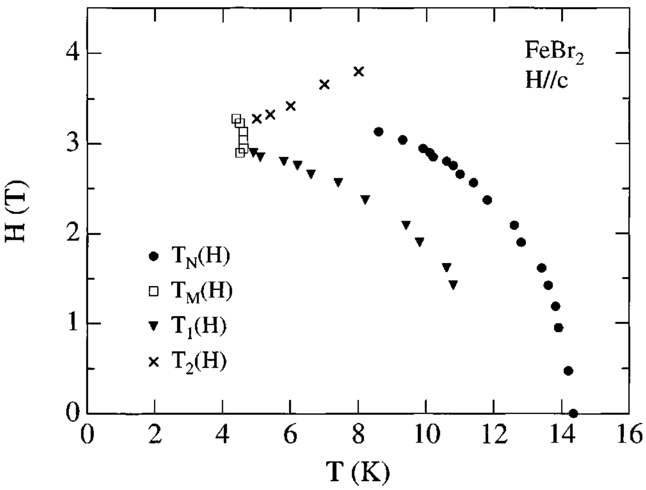

FIG. 2. Magnetic field versus temperature phase diagram of $FeBr_2$ determined by the specific heat measurements.

transition in addition to the AF transition in H. This second peak was clearly observed in H between 1.4 T and 2.9 T. As H is increased, the first peak indicating the AF transition shifts to low temperatures. The second peak shifts to low-temperature side and becomes sharp with the increase of H. It is noted that the shoulder below the second peak becomes prominent as H is increased. In 2.9 T another peak appears just below the second one. Above this field the second peak vanishes. The third peak is observed around 4.6 K up to 3.3 T, which is interpreted as due to the metamagnetic transition based on the H-T phase diagram obtained before.[2] In 3.3 T a very broad peak appears and it shifts to the high-temperature side with further increase of H. We define the transition temperatures as follows: $T_N(H)$ as the temperature giving the C_{mag} maximum which corresponds to the AF transition, $T_M(H)$ to the metamagnetic transition, $T_1(H)$ as the temperature giving the C_{mag} maximum observed below 2.9 T, and at low temperatures, and $T_2(H)$ as the temperature giving the broad maximum observed above 3.3 T.

Figure 2 shows the H-T phase diagram of $FeBr_2$ determined by the present measurement. Each phase boundary seems to merge at the multicritical point. This phase diagram is quantitatively the same as the previous one determined by the magnetization and ac susceptibility measurements.[3] In particular, both temperatures $T_1(H)$ and $T_2(H)$ determined by the present work coincide with the temperatures at which broad maxima in the imaginary part of the ac susceptibility χ'' have been observed. The origin of the χ'' maximum has been explained as due to the strong noncritical fluctuations in the c planes.[3,4,6] The result of the present specific heat measurements, however, indicates that there occurs a phase transition at $T_1(H)$, although the broad peak at $T_2(H)$ does not seem to be critical.

In the following, we investigate theoretically the anomalous behavior of specific heat in $FeBr_2$. Owing to the crystal field and spin-orbit interaction, the lowest state of Fe^{2+} in $FeBr_2$ is a triplet which consists of the lowest doublet and a singlet with a separation by $\sim 10\ \mathrm{cm}^{-1}$ (Ref. 10). The next higher states are separated from the lowest triplet by $\sim 100\ \mathrm{cm}^{-1}$ and may be neglected at low temperatures. From the specific heat data, we estimate the magnetic entropy of $FeBr_2$ at 20 K as 0.69 Nk_B. This means that the contribution from the lowest doublet dominates at low temperatures. Thus an Ising spin model gives a good approximation for describing the magnetic properties of $FeBr_2$ at low temperatures. The interactions of the Ising spins $s_i(=\pm 1)$ are described by the following Hamiltonian:[5]

$$\mathcal{H} = -J_1 \sum_{\langle \mathrm{NN} \rangle} s_i s_j - J_2 \sum_{\langle \mathrm{NNN} \rangle} s_i s_l - J' \sum_{\langle \mathrm{NN}' \rangle} s_i s_k - h \sum_i s_i , \tag{1}$$

where $\langle \mathrm{NN} \rangle$ and $\langle \mathrm{NNN} \rangle$ mean sums over nearest neighbors (NN) and next-nearest neighbors (NNN) in the c plane, respectively, $\langle \mathrm{NN}' \rangle$ means sum over interacting spins belonging to adjacent planes, and $h = g\mu_B H$. The exchange parameters have been determined by the neutron scattering measurement to be $J_1/k_B = 9.3$ K, $J_2/k_B = -3.1$ K, and $J'/k_B = -0.37$ K.[11] The numbers of interacting neighbors are six both for J_1 and J_2. It should be noted that since J' represents the superexchange interaction with ten equivalent paths in each of the neighboring planes, the value of J' obtained in Ref. 11 has been corrected for this number.[4–6] In the following calculations, we set $J_1/k_B = 1$ K for simplicity; however, we make the ratios of the coupling constants realistic. That is, we choose the set of interaction constants as $(J_1/k_B, J_2/k_B, J'/k_B) = (1, -0.3, -0.04)$ in units of K. In zero field $h = 0$, there occurs the antiferromagnetic phase transition at T_N. We call the layers with positive magnetic moments (// H) the A layers and the other ones the B layers. When we apply a positive external field $h > 0$, some spins in the B layers flip. The flip of a spin in the B layers costs the NN$'$ interaction energy but gains Zeeman energy. At low external fields, only a few spins can flip and the flip costs the NN interaction energy but gains the NNN interaction energy. At high fields, only a few spins remain downward and the flips of these spins gain the NN interaction energy. It should be noted that these spin flips cost the NNN interaction energy. In an intermediate strength of external field, therefore, nonuniform spin configurations appear in the B layers due to the competition between the NN ferromagnetic and the NNN antiferromagnetic interactions on the triangular lattices. We expect that the second anomaly in the specific heat observed in our experiments is caused by this competition between the interactions.

In order to study the competition between the NN interaction J_1 and the NNN interaction $-|J_2|$ under the influence of the interlayer interaction $-|J'|$ and an external field h, a mean-field theory is too simple. We have to take into account at least spin pair correlations in our theory. Here we propose a pair approximation following a scheme of the cluster variation method (CVM)[12–14] for the $FeBr_2$ model Eq. (1), in which three kinds of spin pairs interacting with couplings J_1, J_2, and J' are considered. Let $\{s_{A1}, s_{A2}\}$ and $\{s_{A1}, s_{A3}\}$ be pairs of NN and NNN spins in the A layers, respectively. The contributions of these spin pairs to the free energy are given as

$$F_{A2} = -k_B T \ln \left[\sum_{\{s\}} \exp \beta [J_1 s_{A1} s_{A2} + (s_{A1} + s_{A2})(5\lambda_{A1} + 6\lambda_{A2} + 20\lambda_{A'} + h)] \right] \tag{2}$$

and

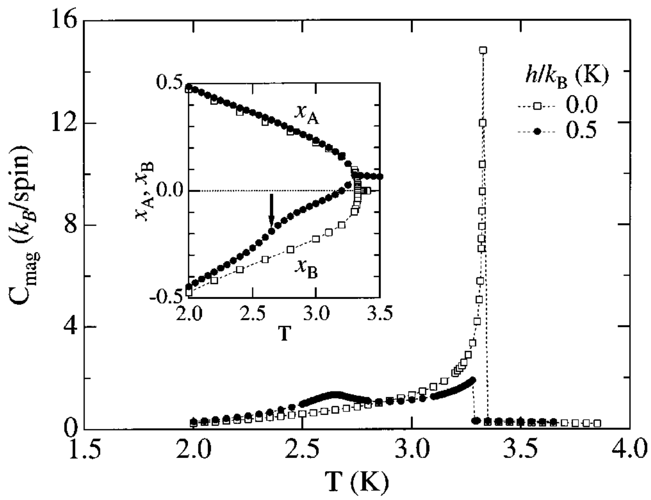

FIG. 3. Magnetic specific heat versus temperature calculated by the pair approximation for the model Eq. (1) with $J_1/k_B = 1$ K, $J_2/k_B = -0.3$ K, and $J'/k_B = -0.04$ K for $h/k_B = 0$ and 0.5 K. In the inset, the temperature dependences of x_A and x_B are shown for $h/k_B = 0$ and 0.5 K, respectively. Arrow indicates an inflection point in x_B for $h/k_B = 0.5$ K.

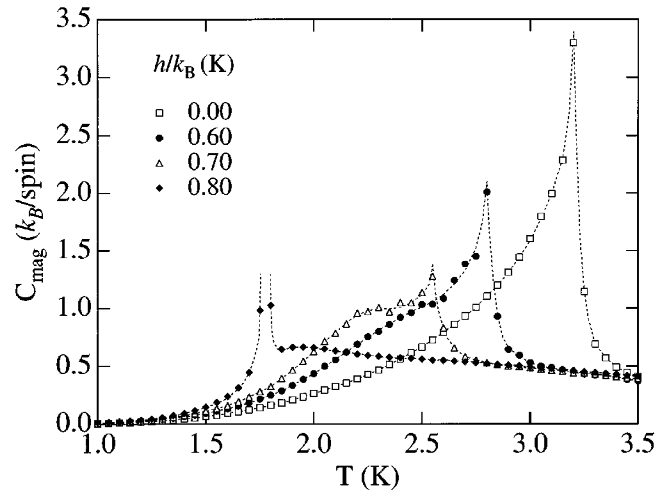

FIG. 4. Results of Monte Carlo simulations for the model Eq. (1) with $J_1/k_B = 1$ K, $J_2/k_B = -0.3$ K, and $J'/k_B = -0.04$ K. Variations of the magnetic specific heat with respect to temperature are shown for the designated fields h. Dotted lines are guides to the eye.

$$F_{A2'} = -k_B T \ln\left[\sum_{\{s\}} \exp\beta[J_2 s_{A1}s_{A3} + (s_{A1}+s_{A3})(6\lambda_{A1} + 5\lambda_{A2} + 20\lambda_{A'} + h)]\right], \tag{3}$$

where the summations are taken over all spin configurations and $\beta = 1/k_B T$. Here λ_{A1} and λ_{A2} are the mean fields from a NN spin and a NNN spin, respectively, and λ'_A is the mean field from a spin in the adjacent B layers. The contribution of a single spin s_{A1} in the A layer to the free energy, F_{A1}, is also given. For spin pairs and a single spin in the B layers, $F_{B2}, F_{B2'}$, and F_{B1} are given in a similar way, where the mean fields $\lambda_{A1}, \lambda_{A2}$, and $\lambda_{A'}$ are replaced by $\lambda_{B1}, \lambda_{B2}$, and $\lambda_{B'}$, respectively. The nearest-neighbor spin pair $\{s_{A1}, s_{B1}\}$ between adjacent layers connected by J' is also considered and its contribution to the free energy is expressed by F_{AB}. Now the free energy per spin is given as

$$f = \tfrac{3}{2}(F_{A2} + F_{A2'} + F_{B2} + F_{B2'}) + 10F_{AB} - \tfrac{31}{2}(F_{A1} + F_{B1}). \tag{4}$$

In the CVM, the mean fields are regarded as variational parameters. Solving the stationary conditions for $\lambda_{A2}, \lambda_{A'}, \lambda_{B2}, \lambda_{B'}$, we can have an expression of the free energy as a function of λ_{A1} and λ_{B1}. The variational principle requires that these parameters λ_{A1} and λ_{B1} should be chosen so that f is minimized and its minimum is the desired value of f at given T and h. Let $x_A = \beta\lambda_{A1}$ and $x_B = \beta\lambda_{B1}$, and we show in the inset in Fig. 3 the temperature dependences of x_A and x_B for $h/k_B = 0$ and 0.5 K.

The magnetic specific heat C_{mag} in a constant field is calculated from f as

$$C_{mag} = -\frac{\partial}{\partial T}\left[T^2 \frac{\partial}{\partial T}\left(\frac{f}{T}\right)\right] - T^2\left[\frac{\partial x_A}{\partial T}\frac{\partial^2}{\partial x_A \partial T}\left(\frac{f}{T}\right) + \frac{\partial x_B}{\partial T}\frac{\partial^2}{\partial x_B \partial T}\left(\frac{f}{T}\right)\right], \tag{5}$$

where the partial differentiation with respect to T is performed in a constant h. We find that C_{mag} has the terms proportional to the derivatives of x_A and x_B with respect to T. The existence of an inflection point in x_B at $T = 2.65$ K for $h/k_B = 0.5$ K (see the inset in Fig. 3) means that $\partial x_B/\partial T$ has a local maximum at this point. It implies that in the external field $h/k_B = 0.5$ K, C_{mag} will have a peak at low temperatures. Figure 3 shows C_{mag} for $h/k_B = 0$ and 0.5 K calculated by Eq. (5) in the present pair approximation. In the absence of external field, C_{mag} shows a sharp gap singularity at $T_N = 3.33$ K and it monotonically decreases as decreasing T below T_N. In a finite field $h/k_B = 0.5$ K, the gap at $T_N = 3.29$ K is comparatively small and we have a local maximum at 2.65 K.

A Monte Carlo simulation was performed by Hernández *et al.* for this $FeBr_2$ model.[5] They studied the antiferromagnetic and metamagnetic phase transitions and calculated the phase diagram on the (T,h) plane. Recently, motivated by the anomalous results of magnetization measurements,[3] Selke and Dasgupta evaluated the derivative of the magnetization with respect to temperature dM/dT and C_{mag} by Monte Carlo simulations for the $FeBr_2$ model.[6] They reported that dM/dT as well as C_{mag} display a broad shoulder or even maximum well below T_N, if a sufficiently high field, e.g., $h = 0.8h_c$, is applied, where h_c is the critical field of the metamagnetic transition. They reported that such anomalous behavior is not reproduced by a mean-field theory. So, our pair approximation is the first analytical calculation which demonstrates the second anomaly in C_{mag}.

We also performed Monte Carlo simulations for various fields. We have studied the $FeBr_2$ model Eq. (1) with $(J_1/k_B, J_2/k_B, J'/k_B) = (1, -0.3, -0.04)$ in units of K on the 16 triangular planes of 32×32 sites with periodic boundary conditions in all three directions. We have adopted the thermal heat method with single-spin flips and the Tausworthe method was used to generate random sequences. Averages were calculated using typically 3×10^4 MCS/spin after having discarded other 3×10^4 MCS/spin to equilibrate the system. The results are shown in Fig. 4. As h is increased, the peak at T_N becomes small and the shoulder appears below T_N. For $h/k_B \geqslant 0.65$ K, we see a local maximum in the shoulderlike region. These results are consistent with the experimental observations that the shoulder appears below the peak at $T_1(H)$ and that it becomes prominent with the increase of the external field. In $h/k_B = 0.8$ K, a sharp peak appears around 1.8 K, which corresponds to the metamagnetic transition.

In conclusion, we have observed, two sharp peaks in specific-heat measurements on $FeBr_2$ in magnetic fields. The present experimental results demonstrate the occurrence of a different kind of phase transition in addition to the well-known antiferromagnetic transition in the intermediate region of external fields below the metamagnetic transition field. Theoretical investigations based on the model Hamiltonian Eq. (1) show that the competition between the nearest-neighbor ferromagnetic and the next-nearest-neighbor antiferromagnetic interactions in the Fe layers manifests its importance in a field under the influence of antiferromagnetic interlayer interactions and this combined effect causes anomalous behavior in the specific heat. It is not yet proved, however, that these ingredients are enough to explain the phenomena, since the second sharp peak observed in the present experiment is not yet reproduced by the calculations.

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