LETTERS

Observation of Magnetic Transition in Quantum Nanomagnet Mn₄Br

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The magnetization of the polycrystalline manganese cluster Mn₄Br was measured down to 0.13 K under a magnetic field of ± 15 kOe. It shows a gradual drop at around 1.5 K and the heat capacity measurement at 0 kOe reveals a sharp anomaly at 1.33 K, indicating the occurrence of a second-order antiferromagnetic (AFM) phase transition. The M–H curve well below the transition temperature T_N shows a step around 2.5 kOe, which probably corresponds to the transition from the AFM phase to metamagnetic (MM) phase. The observed field agrees with that estimated from T_N for the MM transition, using a simple molecular field theory. This is the first observation of a well-defined AFM and also a MM phase among the many manganese clusters with a high-spin ground state that function as molecular nanomagnets.

The magnetic properties of high-spin molecular clusters such as Mn12ac ([Mn₁₂O₁₂(O₂CMe)₁₆(H₂O)₄]) or Fe8 ([Fe₈O₂(OH)₁₂(tacn)₆]⁸⁺, where tacn is the ligand triazacyclononane) have been attracting an increasing interest, since they serve as nanomagnets and show quantum tunneling effects at low temperatures.[1] Recently many examples of high-spin molecular clusters have been reported,[2–5] including several tetranuclear manganese clusters that we reported as exhibiting nanomagnetic behavior.[5] When such a cluster crystallizes into a lattice, the crystal is considered a single array of nanomagnets. Since the organic ligands surrounding the Mn or Fe core separate sufficiently far from each cluster, the intercluster magnetic interactions are generally negligible except the dipole–dipole interactions of the order of 100 Oe for a Mn12ac crystal.[6] However, very recently Bhattacharjee et al. revealed that the intercluster interaction plays an important role in the low temperature magnetic properties of several high-spin tetranuclear manganese clusters.[7] In this paper we report the first observation of an antiferromagnetic (AFM) phase transition, arising from the exchange interaction between the manganese clusters.

Mn₄Br serves as a cation in the crystal of [Mn₄(hmp)₆Br₂(H₂O)₂]Br₂ where hmp is the deprotonated anion of 2-hydroxymethylpyridine.[8] It consists of a planar array of four Mn ions which are of mixed-valence, Mn^{3+}–$(Mn^{2+})_2$–Mn^{3+}. The molecular structure is shown in Fig. 1. Each Mn core is bonded not only to the organic ligands but also to two bromide ions. This means that the tetranuclear manganese core is not perfectly insulated by the organic ligands. The magnetization curve and the high field electron paramagnetic resonance (HFEPR) data indicate that the ferromagnetic intracluster interaction is dominant in each
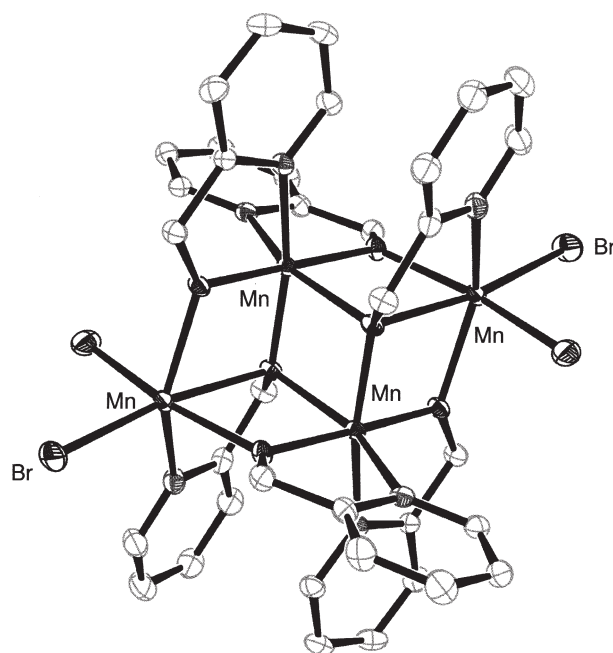

Fig. 1. Molecular structure of Mn₄Br.

cluster, causing a well-isolated high-spin ground state of $S = 9$ below 4 K.[8] The HFEPR spectra are well reproduced assuming $S = 9$ with a large axial zero-field splitting of $D/k_B = -0.498$ K, a small rhombic zero-field splitting of $E/k_B = 0.124$ K and a quadratic longitudinal zero-field splitting of $B_4^0 = 1.72 \times 10^{-5}$ K. The combination of the high-spin multiplicity and the magnetic anisotropy gives rise to a potential barrier of $|DS^2|/k_B = 40.34$ K between the up- and down-spin states.

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The magnetic properties at zero field in the temperature range between 1 K and 4 K were previously investigated by us.[8] The AC susceptibility χ' and χ'' at various frequencies show a blocking behavior, as shown in Fig. 2. The χ' exhibits a gradual drop around 1.5 K, where the out-of-phase signal is observed. The inset of Fig. 2 shows the frequency vs. $1/T_{peak}$ where T_{peak} is a peak temperature of χ''. The peak is considered to arise from freezing of the magnetic moment in each Mn$_4$ cluster, and the plot gives the activation energy $\Delta E/k_B = 15.8$ K, which is reasonable, compared with the $|DS^2|/k_B = 40.34$ K.

The sample was prepared by the method described elsewhere.[8] It was characterized by IR spectrum and chemical analysis data. Magnetization measurements were carried out with a home made Faraday force magnetometer (FFM) installed on a dilution refrigerator. In principle, the FFM detects the Faraday force as a change of capacitance between a rigid electrode and a movable plate on which the sample is mounted. The details of the magnetometer have been described elsewhere.[9] An 80 kOe superconducting magnet with a 100 kOe/m gradient coil (Cryomagnetics Inc.) was used to apply an external magnetic field. A polycrystalline sample of 21.3 mg was glued with a small amount of Apiezon N grease onto an annealed silver foil which was mounted on the movable plate. The other end of the silver foil was tightly fastened with a screw to the annealed silver heat link from the mixing chamber of the dilution refrigerator. The measurement of cerium magnesium nitrate (CMN) with the same experimental setup confirmed a good thermal contact between the sample and the mixing chamber. The temperature was monitored by a carbon and a germanium resistance thermometer attached to the thermal link. The measured static magnetization is shown in Fig. 3 as a function of temperature at various external magnetic fields. It increases with decreasing temperature down to 1.5 K, followed by a gradual drop [Fig. 3(b)]. At 5.0 kOe, the magnetization gradually increases and saturates around 1 K [Fig. 3(a)]. Because there is no hysteresis above 1.0 K for both field cooling and zero-field cooling, it is concluded that
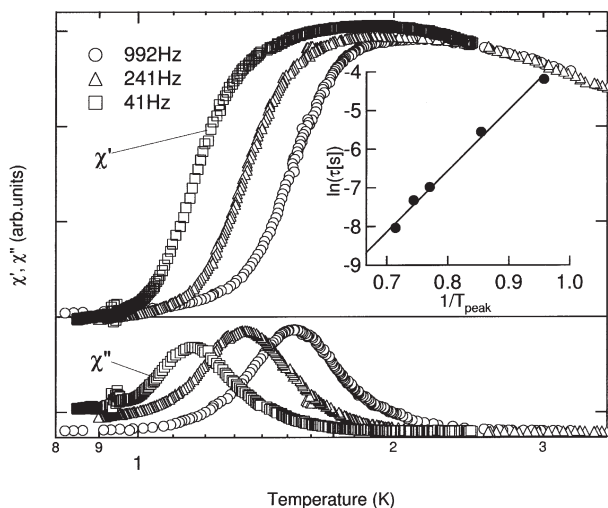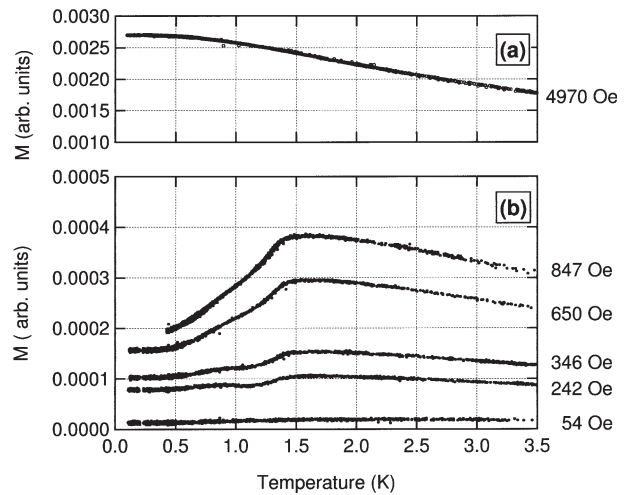

Fig. 3. Temperature dependence of magnetization at various external fields.

the magnetization has a peak at 1.5 K, indicating the antiferromagnetic interaction or antiferromagnetic transition.

To confirm the transition, heat capacity measurements were performed in the temperature range between 0.4 K to 3.5 K with a home made calorimeter by means of the relaxation method.[10] A polycrystalline sample of 17.5 mg was mounted on the copper foil. A heat pulse was added using a resistance heater and then the temperature response was monitored by the other carbon resistance thermometer. The heat capacity was calculated from both the jump and relaxation of the temperature. Figure 4 shows the temperature dependence of the heat capacity measured at zero field. There exists a small shoulder in addition to a gradual increase with increasing temperature. To separate the lattice and the magnetic contribution, we use a Debye model $A \times n \times (T/T_{debye})^3$, where A is the coefficient of 1944 J/K mol, n is the number of atoms contained in a molar unit, 110 [atoms], and T_{debye} is the Debye temperature. Although T_{debye} has not been experimentally obtained for the Mn$_4$Br cluster, there are some reports on T_{debye} for Mn12ac, which was estimated to be 38–41 K.[11,12] The bonding nature of

Fig. 2. Temperature dependence of AC susceptibilities where χ' is the in-phase and χ'' is the out-of-phase components. The inset is an Arrehenius plot of $\tau = 1/2\pi f$ vs $1/T_{peak}$.
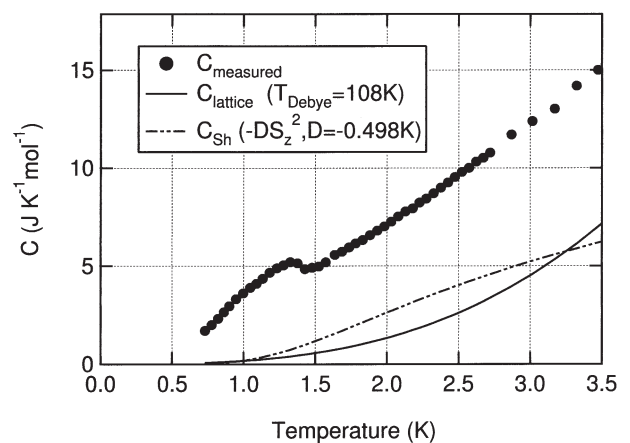

Fig. 4. Temperature dependence of the measured heat capacity, the calculated lattice (solid curve) and the Schottky contributions (dashed curve).

Mn$_4$Br in the cluster is similar to Mn12ac, but the Mn$_4$Br crystal is an ionic one, consisting of Mn$_4$Br and bromide ions, compared with the van der Waals crystal of Mn12ac. Therefore T_{debye} for Mn$_4$Br is supposed to be higher than that for Mn12ac. We tried some analyses assuming T_{debye} to be between 41 and 130 K, and $T_{\mathrm{debye}} = 108$ K was found to give the most reasonable result, because the total magnetic entropy becomes close to $R \ln 2$ at high temperatures (see below). The obtained heat capacity, C_{lattice}, is shown as a solid curve in Fig. 4. We must also take account of the Schottky contribution from the zero-field energy splitting by DS_z^2 above 1 K. The calculated heat capacity, C_{sh}, based on a partition function $Z = \sum \exp(-DS_z^2/k_B T)$, is given as the dashed curve in Fig. 4. Subtraction of C_{lattice} and C_{sh} from C_{measured} gives the heat capacity from the magnetic interaction between Ising-like spins which occupy the two lowest levels ($C_{\mathrm{interaction}}$). As clearly seen in Fig. 5 there exists a sharp anomaly at 1.33 K, indicating the second-order antiferromagnetic phase transition. If this is so, the entropy S can be calculated assuming the spin-wave excitation in Ising antiferromagnets and hence a $\sqrt{a/T}\exp(-a/T)$ law (a: a coefficient) for $C_{\mathrm{interaction}}$ well below T_N.[13] The result is shown in the inset of Fig. 5. The value of S at T_N is 2.46 J/Kmol which is 46% of the maximum entropy of free Ising-like spins, $R \ln 2 = 5.76$ J/Kmol. The small value suggests a certain short-range order is developed even above T_N.

Additional evidence for the AFM phase transition is also obtained by the M–H curve measurements. Figure 6 shows the M–H curves between ± 15 kOe at various temperatures. At 4.2 K, the magnetization curve $M(H)$ is normal, while it shows some anomaly below 1.5 K in accordance with the magnetization peak. At first, the derivative of the magnetization at zero magnetic field tends to decrease. Such a behavior is characteristic of a system in which an antiferromagnetic interaction is dominant. Below T_N, such a tendency becomes clearer, and furthermore, a step is observed at 2.5 kOe. This is not the case of resonant magnetization tunneling for Mn12ac and Fe8, where the steps are usually observed only for sweeping the magnetic field in the opposite direction to the established magnetiza-
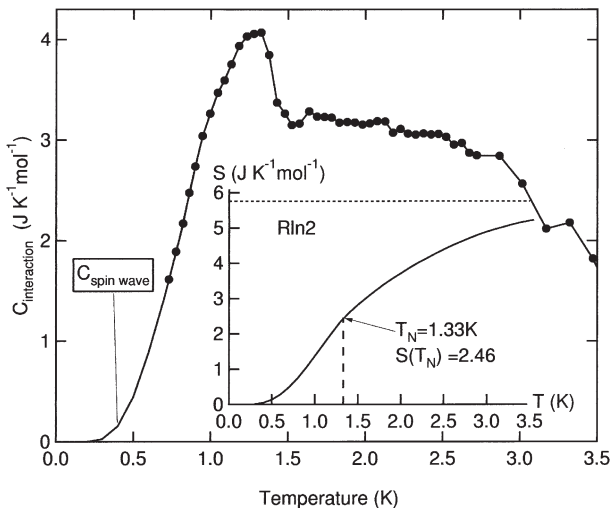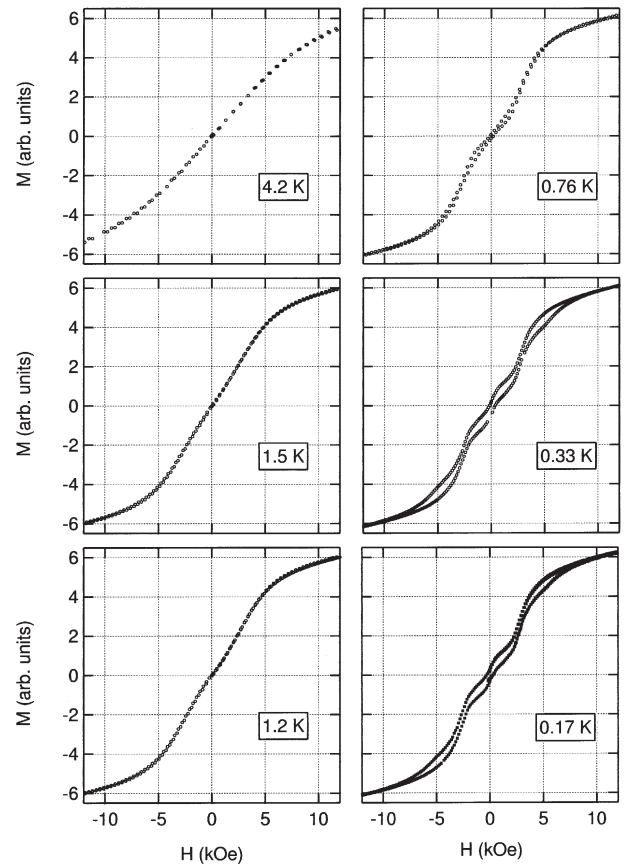

Fig. 6. *M*–*H* curves. The sweep rates are 34 Oe/sec at 4.2 K, 16 Oe/sec at 1.5, 1.2, and 0.76 K, and 6.95 Oe/sec at 0.33 and 0.17 K.

tion. However, the present step is observed at the same field for both increasing and decreasing field. As is well known, an antiferromagnet with a large anisotropy, such as the Ising system, does not show a spin-flop transition but a metamagnetic (MM) one under high magnetic field.[14] Since the Mn$_4$Br cluster has a large anisotropy, $|DS^2|/k_B = 40.34$ K, the step at 2.5 kOe should correspond to a MM transition. In a simple molecular field (MF) approximation, the critical field H_E for the transition from AFM to MM phase at 0 K is calculated as follows,

$$H_E = AM, \quad T_N = \frac{C}{2}(A - \Gamma), \tag{1}$$

where M is magnetization, A and Γ is the summation of the exchange constants J over the nearest neighbor sub lattice and over the next nearest neighbor sub lattice, respectively, and C is a Curie constant. In the case of the dominant nearest neighbor interaction, Γ is approximately zero. The obtained value of H_E from $T_N = 1.33$ K agrees well with the field at which the step occurs in the M–H curves. This strongly suggests the occurrence of a MM phase transition at 2.5 kOe. A small hysteresis observed below 0.9 K is probably due to the first-order nature of the MM transition. In the first-order phase transition the magnetic domain structure exists, causing the hysteresis with variation of the magnetic field.

Now we make some comments on the critical phenomena at T_N. According to a dynamical effective Hamiltonian method, a critical slowing down should increase the relaxation time near T_N by a factor of about 10 compared

Fig. 5. Temperature dependence of heat capacity from contribution of the magnetic interaction.

with the intrinsic relaxation time of each cluster.[15] As shown in Fig. 2, however, there is little anomaly at T_N over the frequency from 1 Hz to 1 kHz, indicating no critical slowing down effect. This is not a rare case in the AFM transition, because the uniform ac field is not the conjugate field of the order parameter of antiferromagnets.[16]

Several high-spin manganese clusters have been reported thus far without any magnetic phase transition. As for the iron clusters, there is a brief statement on the magnetic transition for Fe_4 at about 0.1 K, although the details are not known.[17] Anyway, the observed T_N here is relatively large compared with those for the usual transition metal complex. The estimated transition temperature based on the dipole–dipole interaction is of the order of 30 mK at the largest. The exchange interaction through the bromide ions could play a crucial role on the magnetic order. According to an X-ray structure analysis the crystal forms a one-dimensional chain along the a axis and the intercluster $Br\cdots Br$ contact distance is 4.91 Å.[8] The short-range ordering in this 1D chain possibly brings a large entropy reduction above T_N.

In conclusion, Mn_4Br is found to show the AFM transition at 1.33 K and also the MM transition at the higher magnetic field of 2.5 kOe. Since the large-spin multiplicity, compared to the case of a usual traditional transition metal compound, leads to a large magnetic anisotropy $|DS^2|/k_B = 40.34$ K, the present system is a simple and good model for the Ising spin system. It is interesting to compare the experimental results with theoretical models, especially for the dynamical properties on the phase lines. Therefore, more detailed magnetic measurements should be performed for single crystal or aligned crystalline samples, in order to determine a precise phase diagram and to reveal its dynamical properties.

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