# Topological effects on the magnetic properties of closed and open ring-shaped Cr-based antiferromagnetic nanomagnets

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Topological effects on magnetic properties were revealed by an experimental and theoretical investigation on two Cr-based ring-shaped nanomagnets Cr8 and Cr8Cd as model systems for "closed" and "open" antiferromagnetic rings, respectively. The detailed structures of the low-lying energy levels in terms of the total spin were established directly by high-field magnetization measurements up to 57 T. All the differences observed in the magnetization curve of the two systems can be interpreted by the different topology of the magnetic coupling scheme whereby the experimental observations are well reproduced by theoretical calculations.

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The recent progress in synthesizing molecular nanomagnets gives us the opportunity to investigate magnetic properties of systems composed of a small number of magnetically coupled spins with different topology.[1] Molecular nanomagnets are formed by a small number of transition metal ions with spins embedded in an organic shell so that the magnetic interaction between neighboring molecules is very small. Therefore one can investigate the magnetic properties of an isolated molecular nanomagnet even if powder or bulk samples are used for the measurements.

The antiferromagnetic (AF) ring-shaped system is a particularly interesting subgroup of molecular nanomagnets with a finite number of magnetic ions lying on an almost coplanar ring. Due to the finite-size effect, AF rings have a discrete energy spectrum. The energies of the lowest-lying excited states for the total spin $S_T$ can be approximately given by so-called Lande rule $E(S_T) = (2J/N)S_T(S_T+1)$, where $J$ is antiferromagnetic exchange coupling constant and $N$ is the number of magnetic ions in the ring.[2] The application of external magnetic field lifts the magnetic degeneracy of each $S_T$ state, resulting in successive ground-state level crossings.

One of the best characterized AF ring nanomagnets is $[Cr_8F_8(O_2CC(CH_3)_3)_{16}]0.25C_6H_{14}$ (abbreviated as Cr8)[3] whose ground state is a spin singlet $S_T=0$ state due to AF interaction ($J_{Cr-Cr} \sim 16.9$ K) between nearest-neighbor $Cr^{3+}$ ($s=3/2$) spins.[4] The magnetic interaction between spins is connected to form a "closed" ring as schematically shown in the top part of Fig. 1. On the other hand, owing to recent great success in synthesizing so-called heterometallic AF ring nanomagnets,[5] it becomes possible to change the topology of magnetic interaction of spins in AF ring-shaped nanomagnets. One of the examples is $(Me_2CH)_2NH_2[Cr_8CdF_9(O_2CC(CH_3)_3)_{18}]$ (abbreviated as Cr8Cd)[6] where a $Cd^{2+}$ ($s=0$) ion is added to the eight $Cr^{3+}$ ions of Cr8. Since the $Cd^{2+}$ ion has $s=0$, AF magnetic interaction between nearest-neighbor $Cr^{3+}$ spins is disconnected

by the $Cd^{2+}$ ($s=0$) ion as illustrated in the top of Fig. 1, whereby the system can be regarded as an "open" ring. AF interaction between the $Cr^{3+}$ spins for Cr8Cd is reported to be $J_{Cr-Cr}=14.8$ K from specific heat and magnetic susceptibility measurements.[7]

Both nanomagnets are composed of eight $Cr^{3+}$ spins with the only difference in the boundary conditions (see top of Fig. 1), thus making these nanomagnets ideal model systems to study how the magnetic properties are affected by changing the topology of magnetic coupling. In this Brief Report, we report a comprehensive study of the magnetic properties of the "open" ring (Cr8Cd) and "closed" ring (Cr8) revealed by high-field magnetization measurements at very low temperatures. The observed magnetization processes are well re-
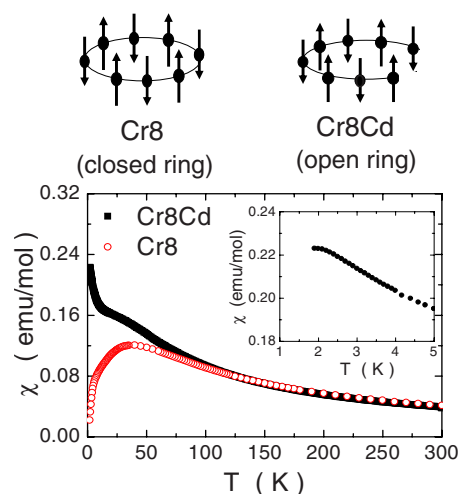


FIG. 1. (Color online) (Top) Schematic views of Cr8 (closed ring) and Cr8Cd (open ring). (Bottom) Temperature dependence of magnetic susceptibility of Cr8 (open circles) at $H=1.28$ T and Cr8Cd (closed squares) at $H=1.0$ T. The inset shows the $T$ dependence of $\chi$ for Cr8Cd in low-temperature region.

produced by theoretical calculations and the differences in the two systems can be explained entirely by the different topology of the magnetic interactions.

The polycrystalline samples of $[Cr_8F_8(O_2CC(CH_3)_3)_{16}]$ $0.25C_6H_{14}$ and $(Me_2CH)_2NH_2[Cr_8CdF_9(O_2CC(CH_3)_3)_{18}]$ were prepared as described in Refs. 3 and 6, respectively. The temperature dependence of the magnetic susceptibility ($\chi$) was measured in a temperature range of $T=1.8-300$ K using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-7T). The magnetization curve was measured using a pulsed magnet up to 57 T and at a temperature below 1 K utilizing $^3He-^4He$ dilution refrigerator at the ISSP of the University of Tokyo. The duration of the pulsed magnetic field is about 6 ms.

The temperature dependence of the magnetic susceptibility $\chi$ for Cr8Cd is shown in the bottom part of Fig. 1, together with the one of Cr8 for comparison. The $T$ dependence of Cr8 agrees with the one reported previously.[3] The broad maximum around 40 K is due to antiferromagnetic interaction between the $Cr^{3+}$ spins. The $\chi$ tends to zero at low temperatures, reflecting the spin singlet ground state. At high temperature, above $\sim100$ K, where each $Cr^{3+}$ spin fluctuates independently, the susceptibility of both rings coincides with each other very well. With decreasing $T$, $\chi$ for Cr8Cd starts to deviate from that of Cr8 below $\sim70$ K and keeps increasing down to 2 K with a shoulder around $\sim40$ K. The $\chi$ in the open ring seems to display a maximum around 2 K as shown in the inset of Fig. 1.

Figures 2(a) and 2(b) show the magnetization ($M$) curves for Cr8Cd ($T=0.5$ K) and Cr8 ($T=0.15$ K), respectively, for increasing magnetic field. In both systems, a clear step-wise increase in magnetization is observed. At low magnetic field, $M$ is observed to be zero for both systems. This is a direct evidence of a singlet ground state for "open" ring Cr8Cd as well as "closed" ring Cr8. Thus the $\chi$ of Cr8Cd is expected to decrease below 2 K and will go to zero at low temperatures due to the singlet ground state. The $M$ rapidly increases step by step with plateaus of $\sim2$ $\mu_B$, $\sim4\mu_B$, $\sim6\mu_B$, ..., at the transition fields $H_n$ ($n=1,2,3,...$). The $H_n$'s were determined by the peak positions of $dM/dH$ curves which are shown by orange lines in Figs. 2(a) and 2(b) for Cr8Cd ($T=0.5$ K) and Cr8 ($T=0.15$ K), respectively. The magnetization curves are nearly the same with no evident hysteresis for the up and down magnetic-field process. On the other hand, we observed butterfly-type hysteresis in magnetization curves for both systems for increasing and decreasing magnetic field at $T=1.3$ K. The hysteresis behavior of the magnetization for Cr8 is shown in Fig. 3, as an example. The observation of the hysteresis behavior of the magnetization originates from nonequilibrium conditions because of the use of a pulsed magnetic field with a few milliseconds duration. Similar hysteresis of the magnetization curve measured utilizing a pulsed magnet have been observed for several magnetic nanomagnets[8–10] and discussed in terms of phonon bottle-neck effects and/or magnetic Föehn effects.[11] It is also interesting to point out in Fig. 2(b) the small increase in $M$ for Cr8 around the middle point in each plateau. This originates from level crossings at excited energy levels. The detailed analysis of the hysteresis behavior observed at $T=1.3$ K and magnetization jump due to the excited energy level crossings will be reported elsewhere.[12]
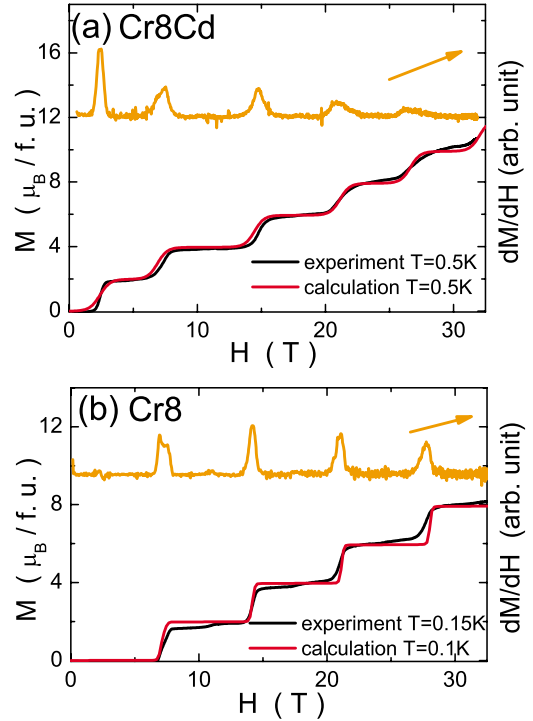


FIG. 2. (Color online) (a) Magnetization curve of Cr8Cd measured at $T=0.5$ K. The red (dark gray) line shows the theoretical calculated result for $T=0.5$ K with the set of parameters: $J_{Cr-Cr}$ $=15.2$ K, $d_{Cr}=-0.3$ K, and $g_{Cr}=1.98$. The orange (gray) line shows the experimental $dM/dH$ curve. (b) Magnetization curve for Cr8 at $T=0.15$ K. The red (dark gray) line is the theoretical calculated result for $T=0.1$ K and parameters: $J_{Cr-Cr}=16.9$ K $d_{Cr}=$ $-0.3$ K, and $g_{Cr}=1.98$. The orange (gray) line shows the experimental $dM/dH$ curve.

The most striking difference between closed ring and open ring is found in the transition fields. The first level crossing field from $S_T=0$ to $S_T=1$ is $\sim7.3$ T for Cr8 and 2.3 T for Cr8Cd. The difference cannot be explained by a small difference of the exchange coupling constants. In addition, the separation of magnetic fields between the level crossing fields defined as $\Delta H_n=H_n-H_{n-1}$ (where $H_0$ is zero) is also different as shown in Fig. 4. $\Delta H_n$ for Cr8 slightly decreases
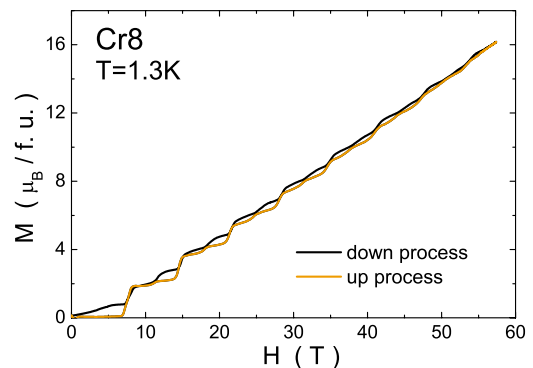


FIG. 3. (Color online) Magnetization curves at $T=1.3$ K for Cr8. The orange (gray) and black lines are for increasing and decreasing field, respectively.
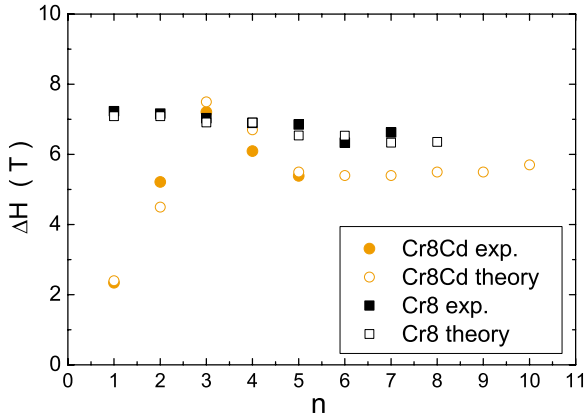
FIG. 4. (Color online) $\Delta H_n$ as a function of $n$. The closed and open symbols show experimental and theoretical results, respectively. The experimental data are taken from the experimental results shown in Fig. 2.

from 7.3 T for $n=1$ to $\sim$6.6 T with increasing $n$. On the contrary, for Cr8Cd, $\Delta H_n$ initially increases from 2.3 T ($n=1$) to 7.2 T ($n=3$) then decreases to 5.4 T ($n=5$).

One can give a simple qualitative explanation for the difference of level crossing fields for the closed and open ring nanomagnets. Let us consider an ideal even-numbered AF ring nanomagnet where each magnetic ion has $s=1/2$ for simplicity. In a closed ring, all spins are coupled to nearest-neighbor spins with AF exchange $J$, with an antiferromagnetic spin structure for $S_T=0$ ground state as illustrated in Fig. 1. In order to flip one of the spins to create the $S_T=1$ state, one needs an excitation energy corresponding to such as $2J$ because each spin is coupled to two spins at either side. On the other hand, in the case of an open ring, the excitation energy depends on the position. When the spin at the edge position is flipped in $S_T=1$ state, the excitation energy could be considered as only $J$ because the flipped spin is coupled to only a spin at one side. The simple model explains qualitatively the experimental observation that the first excitation energy in Cr8Cd is smaller than the one in Cr8 and gives a pictorial view of the edge topological effects.

Another interesting feature expected from the topological effects is the spin moment redistributions in the magnetic ground state. In a closed ring, the excitation energy does not depend on the position so that one can expect uniform spin moment distributions in magnetic ground state. In other words, the excited magnon (so-called triplon) delocalizes in the ring. On the other hand, in the case of the open ring, as the excitation energy depends on the position, spins at the edge position would be polarized easier than in other positions. This can be regarded as a localization of the magnons at the edge position. Thus spin moments depend on the position in the open ring system.

To make the above idea more quantitative, we have carried out theoretical calculations for the Cr-based ring system where each magnetic ion has $s=3/2$. The starting spin Hamiltonian describing the AF ring-shaped clusters is

$$\mathcal{H} = \sum_{i=1}^{m-1} J\mathbf{s}_i \cdot \mathbf{s}_{i+1} + J'\mathbf{s}_8 \cdot \mathbf{s}_1 + \sum_{i=1}^{m} d_{\mathrm{Cr}}\left[ s_z^2 - \frac{1}{3}s(s+1) \right]$$
$$- g_{\mathrm{Cr}}\mu_{\mathrm{B}}\sum_{i=1}^{m} \mathbf{H} \cdot \mathbf{s}_i, \tag{1}$$

where $m$ is the number of magnetic ions (spin). The first and second terms are the isotropic nearest-neighbor Heisenberg interaction. $J'$ is equal to $J$ for Cr8 while $J'$ is assumed to be zero for Cr8Cd because the Cd ions have no spin moment. We also assume that the small next-nearest-neighbor interaction is neglected. The third term describes local crystal field ($d_{\mathrm{Cr}}$ represents a uniaxial anisotropy) and the fourth term represents the Zeeman interaction ($g_{\mathrm{Cr}}$ is $g$-factor for the $\mathrm{Cr}^{3+}$ ions).

The Hamiltonian is diagonalized by following a perturbative procedure described in Refs. 4 and 13. Calculated eigenstates and eigenvalues have been used to evaluate the magnetic-field dependence of the thermal averaged magnetization and the local spin moments. Since we used polycrystalline samples, powder-averaged magnetizations are calculated. With a set of parameters of $J_{\mathrm{Cr-Cr}}=16.9$ K, $d_{\mathrm{Cr}} =-0.3$ K and $g_{\mathrm{Cr}}=1.98$, the magnetization curve for the Cr8 is well reproduced by the calculations [see, Fig. 2(b)]. The $n$ dependence of $\Delta H_n$ is also well reproduced by the theory as seen in Fig. 4. The theoretical estimate of $\Delta H_n$ is done by determining $H_n$ from the peak positions of $dM/dH$ for the calculated powder-averaged $M$. The experimental results for Cr8Cd are also well reproduced by the calculations with the set of parameters: $J_{\mathrm{Cr-Cr}}=15.2$ K, $d_{\mathrm{Cr}}=-0.3$ K, and $g_{\mathrm{Cr}} =1.98$, as shown by the red line in Fig. 2(a). The value of $d_{\mathrm{Cr}}=-0.3$ K is in good agreement with a previously reported value.[7] Interestingly, the peculiar behavior of $\Delta H_n$ in Cr8Cd is almost perfectly reproduced by the calculations as shown by orange open circles in Fig. 4.

As expected, a large difference of distributions for spin moment on different Cr sites in the closed and open nanomagnets is evidenced by the theoretical calculation. In the case of the closed ring Cr8, the spin moment on the Cr ions is zero in $S_T=0$ ground state below first level crossing field of $\sim$7.3 T. Above the crossing field, the Cr ions have a uniform local spin moment of $1/4$ $\mu_{\mathrm{B}}$ for each spin in the $S_T=1$ state, as shown by the dotted line in Fig. 5. This can be interpreted as a consequence of the delocalized traveling triplon with $S=1$. On the contrary, the breaking of the ring symmetry in the open ring Cr8Cd leads to redistributions of spin moments with a staggered spin structure as a consequence of the localized triplon on the edge site. Site dependence of spin moments on Cr ions is shown by solid lines in the figure. Cr ions near the Cd ions possess the largest spin moment, while the spin moment on Cr ions decreases with increasing distance from the Cd ions. Note that spins in Cr8Cd align not uniformly (ferromagnetically) as in Cr8 but staggeringly (antiferromagnetically). These results indicate that the microscopic spin structure in the magnetic ground states is different in the two systems, although the macroscopic total spin moment is the same. To confirm the spin moment distribution from the experimental point of view, a
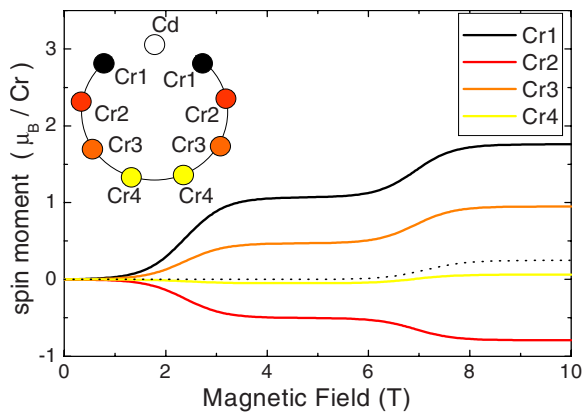
FIG. 5. (Color online) Magnetic-field dependence of thermal averaged local spin moments for Cr8 (dotted line) and Cr8Cd (solid lines) for $T=0.5$ K calculated from Eq. (1). The numbering of Cr sites for Cr8Cd is shown in the inset.

nuclear magnetic resonance (NMR) measurement is one of the most powerful tools.[14] For example, local spin moment for each Cr ion has been revealed by $^{53}$Cr-NMR in an odd-numbered "open" ring nanomagnet Cr7Cd.[15] The $^{53}$Cr-NMR measurements for Cr8 and Cr8Cd are currently in progress.

In conclusion, the magnetic properties of two different antiferromagnetic ring-shaped nanomagnets Cr8 and Cr8Cd have been investigated experimentally and theoretically. Dif-ferent magnetic couplings in the "closed" ring Cr8 and "open" ring Cr8Cd nanomagnets give us opportunities to investigate the role on magnetic properties of spin topology. The spin singlet ground state in Cr8Cd as well as in Cr8 is revealed directly from high-field magnetization measurements below 57 T using a nondestructive pulse magnet in conjunction with a dilution fridge. The energy level structures for quantum total spin state for both systems are directly determined by observation of very clear step-wise increase in the magnetizations. The striking difference of energy structure for the total quantum spin states in the two systems is well understood in terms of topology (in other words, different periodic boundary conditions) and was well reproduced by theoretical calculations based on spin Hamiltonian including a single-ion anisotropy.

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