Magnetic ordering in molecular magnets such as Mn$_{12}$ Ac,$^1$ attracts attention of researchers because the ordering dynamics, as well as domain-wall motion,$^2$ might be intimately related to the spectacular phenomenon of resonance spin tunneling$^3$ under the energy barrier created by the strong uniaxial anisotropy$^4$ acting on the effective spin $S=10$ of the magnetic molecule. The anisotropy barrier is responsible for the bistability of magnetic molecules so that at temperatures below 10 K the latter can be considered as Ising spins $1/2$.* The anisotropy of molecular magnets is a subtle question. The aim of this work is to investigate the possibility of ferromagnetic ordering in its competition with other ordering types in crystals of Mn$_{12}$ Ac of the realistic box shape. While calculations of dipolar fields in crystals of molecular magnets were done for ellipsoids of revolution$^6,^{12}$ that are impossible to grow, no theoretical work has been done yet on box-shape crystals. It is not obvious that long rods behave similarly to long ellipsoids. It was shown that the dipolar field in the middle of the end faces of a uniformly magnetized cylinder of Mn$_{12}$ Ac is opposite to the magnetization (the top of left column of page 4 of Ref. 2). This should lead to spin flips at the ends of the cylinder with a subsequent proliferation into its body. The same can be expected for elongated boxes. Since the dipolar field in crystals of other than ellipsoidal shape is nonuniform, the MFA equations take the form of a large system of equations for all magnetic molecules considered separately.

The model includes pseudospin variables $\sigma_i = \pm 1$ for molecules at each lattice site $i$ of a body-centered tetragonal lattice. The magnetic moment of a molecule is $S g \mu_B$ with $g = 2$. The dipolar field on magnetic molecule $i$ is the sum over positions of all other molecules $j$. In the absence of transverse field, one cannot approach $T_c$ because the relaxation time becomes too long below the blocking temperature 3 K due to the anisotropy barrier. In this case $T_c \approx 0.9$ K was obtained by the linear extrapolation of the $\chi^{-1}(T)$ curve.

Applying a strong transverse field $B_\perp$ up to 6 T (Refs. 7 and 12) increases the relaxation rate via barrier lowering and spin tunneling so that ordering can be achieved during a realistic time$^5$ and the susceptibility measurements can be extended to lower temperatures.$^{12}$ However, the transverse field tends to suppress magnetic ordering and lower $T_c$ via the three main effects: (i) spin canting that reduces the effective magnetic moment along the $z$ axis, (ii) tunneling hybridization of the $|\pm S\rangle$ states that acts as the transverse field in the Ising model that lowers $T_c$ and leads to quantum criticality, and (iii) random longitudinal fields resulting from the strong transverse field and random tilts of the molecular easy axes, further suppressing ordering. These effects have been recently discussed$^{13,14}$ in connection with experiments$^{12}$ on the basis of the mean-field approximation (MFA) that should work well for long-range interactions such as DDI.

The dipolar ordering and the shapes of Mn$_{12}$-acetate crystals

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(Received 23 March 2010; published 18 June 2010)

Ordering in realistic elongated box-shape crystals of the molecular magnet Mn$_{12}$ Ac is investigated with the site-resolved mean-field approximation that does not assume a uniform ordering. It is shown that uniform ferromagnetic ordering does not occur in crystals with the aspect ratio up to 12. Instead, ordering resembling ferromagnetic ordering with domains is realized. Finding ordering temperature by linearly extrapolating the inverse susceptibility curve above the transition temperature does not provide a correct $T_c$.
Here $D_{zz}$ is the reduced dipolar field and

$$\phi_{ij} = \frac{3(\mathbf{e}_i \cdot \mathbf{n}_{ij})^2 - 1}{r_{ij}}, \quad \mathbf{n}_{ij} = \frac{r_{ij}}{r_{ij}}$$

Inside a uniformly magnetized ellipsoid, $\sigma = \text{const}$, the dipolar field is uniform and one has $D_{zz} = D_{zz} \sigma_z$, where

$$D_{zz} = D_{zz}^{(\text{ph})} + 4 \pi r^2 / n^{(2)}^2,$$

$\nu$ is the number of magnetic molecules per unit cell ($\nu = 2$ for Mn$_{12}$ Ac) and $n^{(2)} = 0$, 1/3, and 1 for a cylinder, sphere, and disk, respectively. The reduced dipolar field in a sphere $D_{zz}^{(\text{ph})} = 52.6$ mT in an elongated sample that was also obtained experimentally. The ground-state energy in the above uniform states is given by

$$E_0 = -\langle 1/2 \rangle D_{zz} E_D, \quad E_D = (S g \mu_B)^2 / v_0,$$

where $E_D$ is the dipolar energy, $E_D/k_B = 0.0671$ K for Mn$_{12}$ Ac. The mean-field Curie temperature is given by

$$T_C = E_D D_{zz} / k_B$$

that results in $T_C = 0.707$ K.

States with ferromagnetically ordered planes alternating in the $a$ or $b$ directions in each sublattice of Mn$_{12}$ Ac have $D_{zz} = 9.480$, independently of the sample shape. The state with alternating chains in each sublattice, directed along the $c$ direction has a very close value $D_{zz} = 9.475$. For the two-sublattice antiferromagnetic ordering one obtains $D_{zz} = 8.102$. Thus, in a strongly prolate ellipsoid of Mn$_{12}$ Ac magnetic ordering is preferred. It is interesting to estimate how strongly the prolate ellipsoid has to be for this to be the case. Equating $D_{zz}$ of Eq. (3) to $D_{zz} = 9.480$ for the alternating-plane structures, one obtains the maximal demagnetizing factor $n^{(2)} = 0.0419$. Using the formula for prolate ellipsoids of revolution, one obtains that the minimal shape aspect ratio $R_a / R_c = 6.13$ is required for ferromagnetic ordering.

The longest crystal used in the experiments of Ref. 12 has dimensions $0.4 \times 0.4 \times 2.4$ mm$^3$ and thus the aspect ratio 6 that would be still slightly insufficient for a crystal of ellipsoidal shape to order ferromagnetically. We will see below that even much longer box-shape Mn$_{12}$ Ac crystals do not show a uniform ferromagnetic order. The reason for this should be the above-mentioned instability of the ferromagnetic ordering at the ends driven by the negative value of the dipolar field, $D_{zz} = -2.03$.3

The system of Curie-Weiss equations for a crystal of molecular magnet in a uniform external field $B_z$ has the form

$$\langle \sigma_z \rangle = \tanh \left( \frac{E_D/k_B}{T} \sum_{i,j} \phi_{ij} (\sigma_z) r_{ij} + h_z T \right),$$

where $h_z = S g \mu_B B_z / k_B$. The linearized Curie-Weiss equations above $T_c$ can be cast into the matrix form

$$(T_I - V) \langle \sigma_z \rangle = h_z \mathbf{I}.$$
DIPOLAR ORDERING AND THE SHAPES OF Mn$_{12}$-

FIG. 1. (Color online) Inverse susceptibility of elongated box-shape crystals of Mn$_{12}$ Ac vs temperature. While the $\chi^{-1}(T)$ curves extrapolate to the would be ferromagnetic ordering temperatures, the real ordering occurs at a higher temperature and is not uniform ferromagnetic.

Numerical calculations show that the uniform-field coupling coefficient $(A^{L}_{\mu} I)(A^{R}_{\mu} I)$ reaches large values for a narrow group of $\mu$ around some $\mu_{\text{ferro}}$ while for other $\mu$ values $(A^{L}_{\mu} I)(A^{R}_{\mu} I)$ are much smaller. The eigenvectors $A^{L}_{\mu}$ have all their elements of the same sign while other eigenvectors have elements of different signs and do not project well on the uniform field. Thus not too close to $T_C$ Eq. (8) is dominated by a narrow group of ferromagnetic terms that result in nearly linear dependence $\chi^{-1}(T) \propto T - T_{\text{ferro}}$ that extrapolates to $T_{\text{ferro}}$ as an apparent transition temperature. In all cases for which numerical calculations have been performed, it turns out that $T_{\text{ferro}} < T_C$ and thus $T_C$ corresponds to other types of ordering than uniform ferromagnetic. (As we will see below, the actual ordering is ferromagnetic with domains.) As $T$ approaches $T_C$, the term with $T_{\mu} = T_C$ in Eq. (8) becomes dominant and the curve $\chi^{-1}(T)$ drops suddenly to zero. Of course, the behavior shown in Fig. 1 for several different crystals cannot be seen and actual $T_C$ cannot be found, if only the high-temperature susceptibility data are available, as in Ref. 12. In fact, there are many different ordering eigenvalues $T_{\mu}$ in the region between $T_{\text{ferro}}$ and $T_C$.

It appears that with increasing the crystal size coupling of the uniform field to nonferromagnetic eigenvectors decreases so that the drop of $\chi^{-1}(T)$ at $T_C$ becomes sharper. This makes using uniform susceptibility to detect $T_C$ in the case of a nonferromagnetic ordering questionable. Of course, theoretically one can couple to the nonferromagnetic ordering modes by a nonuniform magnetic field (such as the staggered field in the case of antiferromagnetism) but practically it is difficult to realize.

FIG. 2. (Color online) Magnetization of elongated box-shape crystals of Mn$_{12}$ Ac of different dimensions, developing upon lowering temperature at a slow constant rate. Static inverse susceptibility for $L_a=8$, $L_c=50$ from the preceding figure is also shown.

FIG. 3. (Color online) Ordering in elongated box shape Mn$_{12}$ Ac crystals ($L_a=8$, $L_c=50$) at $T=0$, obtained by slow lowering temperature from $T_{\text{max}} > T_C$ and shown in the cross section through the middle of the crystal. (a) Sublattice 1 and (b) sublattice 2. Magnetization in both sublattices is qualitatively similar. Magnetization at $T=0$ is uniform along the $c$ direction.

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One can see from Fig. 1 that $T_{\text{ferro}}$ essentially depends on the aspect ratio, as it should be, and is in accord with Eq. (3). To the contrary, $T_C$ does not strongly depend on the shape since it does not correspond to the uniform ferromagnetic ordering. Its moderate increase with the crystal size shows that the crystal sizes in the numerical calculations are still somewhat small to perfectly reproduce the behavior of macroscopic crystals. With increasing elongation, uniform ferromagnetic ordering becomes more competitive but still falls behind other orderings up to the aspect ratios of about 12 where ellipsoids would already order ferromagnetically. It is difficult to increase the elongation while keeping the transverse size large enough in the calculations because the number of molecules becomes too large.

Note that in the case of the standard antiferromagnetism the ferromagnetic eigenvalue $T_{\text{ferro}}$ is negative. The ferromagnetic state in the antiferromagnet is absolutely unstable, as the molecular field is opposite to the spins. In our problem of dipolar ordering, there are many positive and many negative eigenvalues $T$. Negative $T$ corresponds to absolutely unstable states, whereas $T > 0$ corresponds to local minima of energy with dipolar fields parallel to spins.

Competition of many local energy minima in our model of ordering in Mn$_{12}$Ac makes it impossible to describe the ordered state below $T_C$ by solving Eq. (6) directly. Instead of the global minimum of the free energy, the solver finds local minima, local maxima, or saddle points. A more reliable method is to solve the system of relaxation equations

$$d(\sigma_z)/dt = -\Gamma[(\langle\sigma_z\rangle - \tanh(\cdots))]$$

where $\Gamma$ is the relaxation rate and $\tanh(\cdots)$ is the same as in Eq. (6). As the purpose of this work was to study ordering rather than the exact dynamics, $\Gamma$ was set to an arbitrary constant in numerical calculations. It was found that Eq. (9) leads to freezing into a spin-glass state as the result of relaxation out of a random initial state at low temperatures. To obtain the ordering type that is mostly close to the lowest free-energy state at any temperature, one can solve Eq. (9) with temperature $T$ slowly changing in time from some $T_{\text{max}} > T_C$ to nearly zero. Just to initiate ordering, one can set $h$ to a very small value.

Figure 2 shows the results of these calculations for two different crystal sizes. The $\langle\sigma_z\rangle$ curves accurately reproduce the equilibrium magnetization everywhere except for the critical region ($0.6 \text{ K} \leq T \leq 0.7 \text{ K}$) where critical slowing down reduces to a slower temperature sweep that is difficult to implement in the numeric routine. The average magnetization at $T=0$ in both cases is significantly smaller than 1 because of the nonuniform ordering. A nonzero average magnetization in the ordered state seems to be the effect of the algorithm still not finding the deepest energy minimum. Ordering attained at $T=0$ is shown in Fig. 3 for cross sections through the middle of the crystal length. In fact, the magnetization at $T=0$ is uniform along the $c$ axis. One can see that the regions of the same orientation of spins are greater than the lattice period and both sublattices are magnetized in a similar way, up to finite-size effects.

Concluding, mean-field calculations do not support uniform ferromagnetic ordering in elongated box-shape crystals of Mn$_{12}$Ac that are currently under investigation. How long box-shape crystals must be to order ferromagnetically remains an open question.

Useful discussions with E. M. Chudnovsky, A. D. Kent, M. P. Sarachik, Y. Yeshurun, and A. J. Millis are gratefully acknowledged. I have profited from having access to the experimental data by A. D. Kent, M. P. Sarachik, Y. Yeshurun, Bo Wen, and other team members during the experiments. This work has been supported by the NSF under Grant No. DMR-0703639.