

Dipolar ordering and the shapes of Mn_{12} -acetate crystals

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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 .

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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 tunneling³ under the energy barrier created by the strong uniaxial anisotropy⁴ 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 pointing up or down. Mn_{12} Ac crystallizes into a body-centered tetragonal lattice with the periods $a=b=17.319$ Å and $c=12.388$ Å, c being the direction of the magnetic easy axis z . The unit-cell volume is $v_0=abc=3716$ Å³ and there are two molecules per unit cell, $\nu=2$.

Since the magnetic core of magnetic molecules is surrounded by organic ligands, there is practically no exchange interaction between the molecules. Thus the sole source of magnetic ordering is the dipole-dipole interaction (DDI) that leads to ordering below 1 K in Fe_8 (Refs. 5 and 6), Mn_{12} Ac (Ref. 7), and other compounds.^{8–11} The type of dipolar magnetic ordering in molecular magnets is a subtle question. Since a column of spins up directed along the c axis produces a magnetic field up on its own spins that largely exceeds the field it produces on other spins,⁵ one concludes that the ground state includes ferromagnetically ordered columns along the c axis. The ferromagnetic columns can order ferromagnetically or antiferromagnetically with respect to each other.

It was shown that the ground state of ellipsoids of revolution depends on their aspect ratio.² For ellipsoids very prolate along the c axis, the ground state was found to be ferromagnetic, whereas in other cases there are ferromagnetic columns or planes ordered antiferromagnetically with respect to each other. The energies of differently ordered states are rather close so that practically the system will order in a spin-glass state upon fast cooling.

Evidence for a ferromagnetic ordering in Mn_{12} Ac was obtained in Ref. 7 by neutron-scattering experiments. However, the shape of the crystal was not specified. Usually crystals of molecular magnets are box shaped and elongated along the c axis but it is a question if they are elongated enough to make ferromagnetic ordering prevail. Recent measurements of the ferromagnetic susceptibility χ above T_C in Mn_{12} Ac and its modifications¹² were done on box-shape single crystals with the aspect ratio L_c/L_a of about 5–6. 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 time⁷ 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 experiments¹² on the basis of the mean-field approximation (MFA) that should work well for long-range interactions such as DDI.

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^{2,6,13} 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 $Sg\mu_B$ with $g=2$. The dipolar field on magnetic molecule i is the sum over positions of all other molecules j

$$B_{i,z}^{(D)} = \frac{Sg\mu_B}{v_0} D_{i,zz}, \quad D_{i,zz} \equiv \sum_j \phi_{ij} \sigma_{jz}. \quad (1)$$

Here D_{zz} is the reduced dipolar field and

$$\phi_{ij} = v_0 \frac{3(\mathbf{e}_z \cdot \mathbf{n}_{ij})^2 - 1}{r_{ij}^3}, \quad \mathbf{n}_{ij} \equiv \frac{\mathbf{r}_{ij}}{r_{ij}}. \quad (2)$$

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

$$\bar{D}_{zz} = \bar{D}_{zz}^{(\text{sph})} + 4\pi\nu(1/3 - n^{(z)}), \quad (3)$$

ν is the number of magnetic molecules per unit cell ($\nu=2$ for Mn_{12} Ac) and $n^{(z)}=0, 1/3$, and 1 for a cylinder, sphere, and disk, respectively. The reduced dipolar field in a sphere $\bar{D}_{zz}^{(\text{sph})}$ depends on the lattice structure. For Mn_{12} Ac direct lattice summation yields $\bar{D}_{zz}^{(\text{sph})}=2.155$ that results in $\bar{D}_{zz}^{(\text{cyl})}=10.53$ for a cylinder.² Then Eq. (1) yields the dipolar field $B_z^{(D)} \approx 52.6$ mT in an elongated sample that was also obtained experimentally.¹⁵ The ground-state energy in the above uniform states is given by

$$E_0 = -(1/2) \bar{D}_{zz} E_D, \quad E_D \equiv (Sg\mu_B)^2 / v_0, \quad (4)$$

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 by²

$$T_C = E_D \bar{D}_{zz} / k_B \quad (5)$$

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

The longest crystal used in the experiments of Ref. 12 has dimensions $0.4 \times 0.4 \times 2.4$ mm³ 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, $\bar{D}_{zz}=-2.03$.²

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

$$\begin{aligned} \langle \sigma_{iz} \rangle &= \tanh \frac{Sg\mu_B(B_{i,z}^{(D)} + B_z)}{k_B T} \\ &= \tanh \left(\frac{E_D/k_B}{T} \sum_j \phi_{ij} \langle \sigma_{jz} \rangle + \frac{h_z}{T} \right), \end{aligned} \quad (6)$$

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

$$(T\mathbf{I} - \mathbf{V}) \cdot \langle \sigma_z \rangle = h_z \mathbf{I}. \quad (7)$$

Here \mathbf{V} is the DDI matrix, $\{V\}_{ij} = (E_D/k_B) \phi_{ij}$, \mathbf{I} is a unit matrix, $\{I\}_{ij} = \delta_{ij}$, and \mathbf{I} is a unit vector, $\{I\}_i = 1$. In fact, position of a molecule in the lattice is defined by three numbers i_a, i_b , and i_c corresponding to the three directions a, b , and c plus the sublattice index. The indices i, j are compound indices running from 1 to the number of sites in the lattice N . In terms of i, j the matrix \mathbf{V} is nonsymmetric so that care should be taken by distinguishing between its right and left eigenvectors. One can seek the solution in the form $\langle \sigma_z \rangle = \sum_\mu C_\mu \mathbf{A}_\mu^R$, where \mathbf{A}_μ^R are right eigenvectors, $\mathbf{V} \cdot \mathbf{A}_\mu^R = T_\mu \mathbf{A}_\mu^R$, and T_μ are eigenvalues, $\mu=1, \dots, N$. The right and left eigenvectors satisfy the orthonormality condition $\mathbf{A}_{\mu'}^L \cdot \mathbf{A}_\mu^R = \delta_{\mu'\mu}$, i.e., the matrix of left eigenvectors is the inverse of that of the right eigenvectors. Using the orthonormality, from Eq. (7) one obtains $C_\mu = (\mathbf{A}_\mu^L \cdot \mathbf{I}) h / (T - T_\mu)$. For the susceptibility of the whole crystal $\chi = (1/N) (\langle \sigma_z \rangle \cdot \mathbf{I}) / h_z$ one finally obtains

$$\chi = \frac{1}{N} \sum_{\mu=1}^N \frac{(\mathbf{A}_\mu^L \cdot \mathbf{I})(\mathbf{A}_\mu^R \cdot \mathbf{I})}{T - T_\mu}. \quad (8)$$

Thus defined susceptibility has the unit K⁻¹. To obtain the standard magnetic susceptibility dM/dB_z , one has to add the factor E_D/k_B in Eq. (8). The ordering temperature T_C can be identified with the maximal of the eigenvalues T_μ .

Numerical calculations have been done using Wolfram Mathematica for box-shape crystals of dimensions $L_a=L_b \ll L_c$ in units of the lattice spacing a . The numbers $L_a=L_b$ and L_c have been taken even. The indices i_a and i_b specifying positions of molecules within the a, b plane run in the range $-i_{a,b,\text{max}} \leq i_{a,b} \leq i_{a,b,\text{max}}$ for sublattice 1 and in the range $-i_{a,b,\text{max}} + 1/2 \leq i_{a,b} \leq i_{a,b,\text{max}} - 1/2$ for the body-centered sublattice 2, where $i_{a,b,\text{max}} = L_a/2$. For the crystallographic direction c , the index ranges are $-i_{c,\text{max}} \leq i_c \leq i_{c,\text{max}}$ and $-i_{c,\text{max}} + 1/2 \leq i_c \leq i_{c,\text{max}} - 1/2$, respectively, where $i_{c,\text{max}} = \text{Round}[L_c/(2\eta)]$ and $\eta = c/a = 0.7153$ for Mn_{12} Ac. The total number of molecules in the crystals studied thus is given by $N = (2i_{a,\text{max}} + 1)(2i_{b,\text{max}} + 1)(2i_{c,\text{max}} + 1) + (2i_{a,\text{max}})(2i_{b,\text{max}})(2i_{c,\text{max}})$ that reached $N=31\,061$ for the biggest crystal with $L_a=L_b=10$ and $L_c=100$. However, the actual number of lattice sites in the calculations was reduced by a factor of approximately 8 by using symmetry that resulted in the gain of approximately $8^2=64$ in the computer time and memory usage.

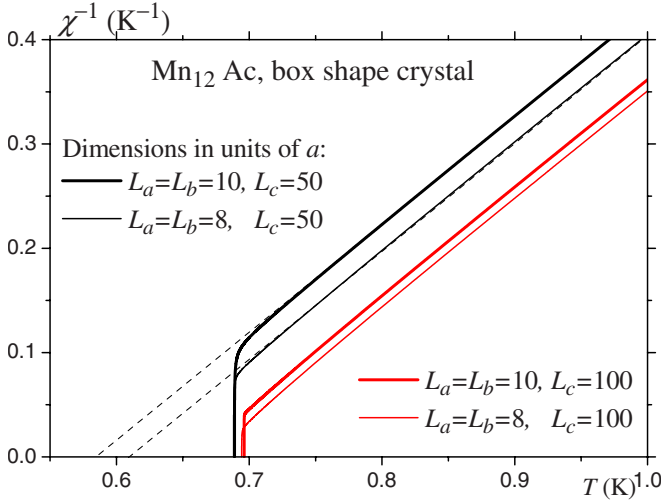


FIG. 1. (Color online) Inverse susceptibility of elongated box-shape crystals of Mn_{12}Ac vs temperature. While the $\chi^{-1}(T)$ curves extrapolate to the would be ferromagnetic ordering temperatures, the real ordering occurs at a higher temperature and is not uniform ferromagnetic.

Numerical calculations show that the uniform-field coupling coefficient $(\mathbf{A}_\mu^L \cdot \mathbf{I})(\mathbf{A}_\mu^R \cdot \mathbf{I})$ reaches large values for a narrow group of μ around some μ_{ferro} while for other μ values $(\mathbf{A}_\mu^L \cdot \mathbf{I})(\mathbf{A}_\mu^R \cdot \mathbf{I})$ are much smaller. The eigenvectors $\mathbf{A}_\mu^{L,R}$ 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_{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

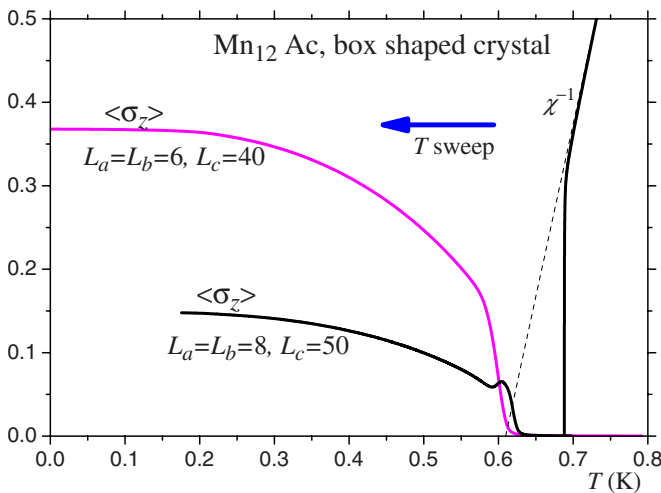


FIG. 2. (Color online) Magnetization of elongated box-shape crystals of Mn_{12}Ac of different dimensions, developing upon lowering temperature at a slow constant rate. Static inverse susceptibility for $L_a=L_b=8, L_c=50$ from the preceding figure is also shown.

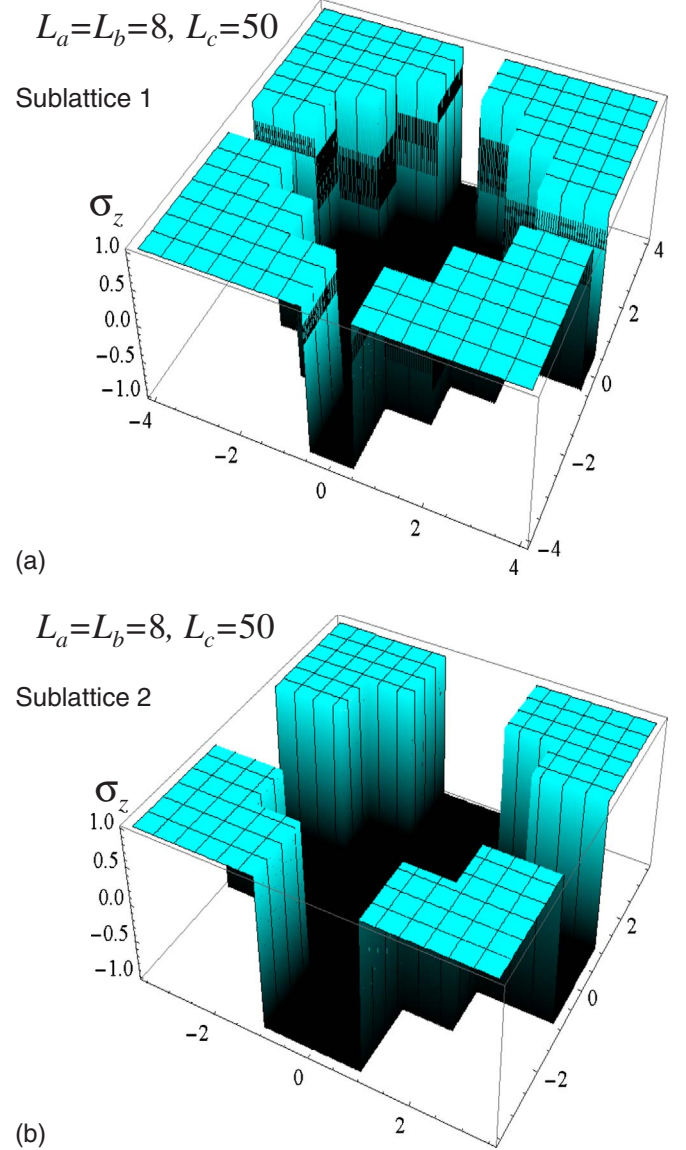


FIG. 3. (Color online) Ordering in elongated box shape Mn_{12}Ac crystals ($L_a=L_b=8, L_c=50$) at $T=0$, obtained by slow lowering temperature from $T_{\text{max}} > T_C$ and shown in the cross section through the middle of the crystal. (a) Sublattice 1 and (b) sublattice 2. Magnetization in both sublattices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

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_μ in the region between T_{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.

One can see from Fig. 1 that T_{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_{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_μ . Negative T_μ corresponds to absolutely unstable states, whereas $T_\mu > 0$ 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 relaxational equations

$$d\langle\sigma_{iz}\rangle/dt = -\Gamma[\langle\sigma_{iz}\rangle - \tanh(\cdots)], \quad (9)$$

where Γ 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, Γ 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 relax-

ation 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_z 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 requires a slower temperature sweep that is difficult to implement in the numeric routine. The average magnetization at $T \rightarrow 0$ 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 $T \rightarrow 0$ is shown in Fig. 3 for cross sections through the middle of the crystal length. In fact, the magnetization at $T \rightarrow 0$ 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.¹² How long box-shape crystals must be to order ferromagnetically remains an open question.

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