

Macroscopic evidence of quantum coherent oscillations of the total spin in the Mn-[3 × 3] molecular nanomagnet

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Abstract. Molecular nanomagnets, besides promising to open new frontiers in technology, have attracted huge interest in the scientific community because they can exhibit the phenomenon known as quantum tunnelling of the magnetization, i.e. coherent fluctuations of the direction of the total spin vector. In this paper we study a different quantum phenomenon involving fluctuations of the magnitude of the total spin vector. These fluctuations are related to the mixing between states with different spin quantum number, and imply new macroscopic effects, which we theoretically investigated in the Mn-[3 × 3] grid.

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Molecular nanomagnets (MNMs) [1–3] are clusters containing a finite number of transition-metal ions whose magnetic moments (spins) are so strongly coupled that at low temperature each molecule behaves like a single-domain particle with fixed total spin. Being at the crossover between classical and quantum regimes, MNMs exhibit at the same time classical properties of macroscopic magnets such as magnetization hysteresis, and quantum phenomena like tunneling of the direction of the total spin through energy barriers [4–6]. MNM systems are interesting also for potential technological applications, as envisaged for the implementation of quantum computing algorithms [7], or for dense and highly efficient memory devices [1]. Here we study a new macroscopic manifestation of a quantum phenomenon involving fluctuations not only of the direction, but also of the magnitude of the total spin, and we show that it is realized in a Mn-[3 × 3] grid [8,9]. Recognizing the effects of these fluctuations is essential to achieve a satisfactory understanding of the role played by quantum mechanics in complex mesoscopic magnetic systems. Quantum magnetic phenomena were identified even in molecules of great biological interest such as ferritin [10,11].

The advantage of studying quantum phenomena in MNMs is that the vanishingly small interaction between different molecules allows single-molecule phenomena to be observed at a macroscopic scale, because the crystal behaves like a collection of independent objects [2,12], each

described in general by spin Hamiltonians of the form [13]

$$H = \sum_{i>j} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j + \sum_i \mathbf{s}_i \cdot \mathbf{D}_i \cdot \mathbf{s}_i + \sum_{i>j} \mathbf{s}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{s}_j + \mu_B \sum_i g_i \mathbf{B} \cdot \mathbf{s}_i, \quad (1)$$

where \mathbf{s}_i are spin operators of the i th ion in the molecule. The first term is the isotropic Heisenberg exchange interaction, the second and third terms describe the local crystal-field and the anisotropic intra-cluster spin-spin interactions. The last term is the Zeeman coupling with an external field \mathbf{B} in which isotropic g -factors are assumed. While the Heisenberg term is rotationally invariant and therefore conserves the length $|\mathbf{S}|$ of the total spin $\mathbf{S} = \sum_i \mathbf{s}_i$, the anisotropic terms break rotational invariance and do not conserve this observable. Nevertheless, since the Heisenberg contribution is usually largely dominant, $|\mathbf{S}|$ is nearly conserved, and the energy spectrum of H consists of a series of level multiplets with an almost definite value of $|\mathbf{S}|$ (expressed in terms of the quantum number S as $\sqrt{S(S+1)}$). Thus, quantum fluctuations of $|\mathbf{S}|$, which are associated with mixing of states with different value of the quantum number S (“ S -mixing” [14]), either are zero or are expected to produce negligible effects on the macroscopic behavior, and are therefore neglected in virtually all studies. A major theoretical goal would be to identify a clear macroscopic signature of such fluctuations, and a model system displaying such effect.

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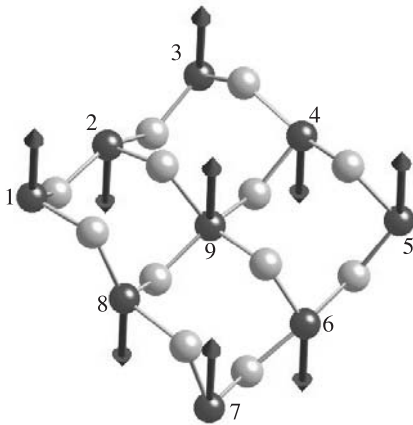


Fig. 1. A schematic representation of the molecular structure of the Mn-[3×3] grid showing the network of manganese (dark) and oxygen (bright) bonds. Other atoms are omitted for clarity. Arrows indicate the spin directions in the classical ground state.

In this paper we show that favorable conditions are met in the Mn(II)-[3×3] grid-like cluster $[\text{Mn}_9(2\text{POAP-2H})_6](\text{ClO}_4)_6 \cdot 3.57\text{MeCN} \cdot \text{H}_2\text{O}$ (hereafter Mn-[3×3], see Fig. 1), a system that has been recently characterized by magnetization and torque measurements [9,15]. Our theoretical calculations suggest grid-shaped molecules as good candidates to study fluctuations of $|\mathbf{S}|$, since the lowest level is expected to display significant S -mixing with the first excited multiplet. In fact, unlike in ideal ring-shaped molecules [16], in the [3×3] grid the two lowest manifolds of the exchange part of the spin Hamiltonian belong to the same irreducible representation of the molecular symmetry group. Therefore, the application of a suitably oriented magnetic field induces a series of anticrossings (ACs) between the ground state and levels originating from higher excited manifolds (see Fig. 2). At the AC fields, S -mixing in the ground state is maximum, and quantum fluctuations of $|\mathbf{S}|$ are greatly enhanced. Torque [9] and neutron [17] experiments on Mn-[3×3] show that the zero-field gap between the two lowest S -multiplets is small enough for the ACs to occur at fields within experimental reach.

Mn-[3×3] crystallizes in the space group C_2/c , and the cation $[\text{Mn}_9(2\text{POAP-2H})_6]^{6+}$ exhibits a slightly distorted S_4 molecular symmetry with the C_2 axis perpendicular to the plane of the cluster [8]. The average distance between the Mn(II) ions is 3.93 Å, the smallest distance between clusters is larger than 8 Å. For a cluster composed of nine interacting Mn(II) spins with $s_i = 5/2$ the dimension of the Hilbert space is 10077696. The difficulties related with this huge dimension have been overcome by exploiting both the irreducible tensor operator technique and the Lanczos algorithm for the exact diagonalisation. The two-step procedure already developed [18] has allowed the inclusion of S -mixing effects in the calculation. The exchange integrals and the single-site and spin-spin anisotropy tensors have been determined by neutron spectroscopy [17]. All exchange integrals between nearest-neighbors are found to be nearly equal to 0.47 meV, apart

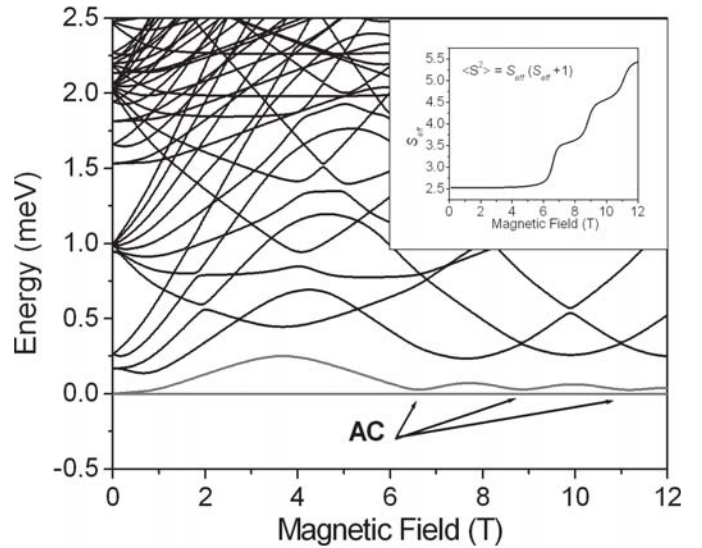


Fig. 2. Calculated energy levels of the Hamiltonian (Eq. (1)) with the parameters given in the text, and with the direction of the applied field forming an angle $\theta = 2.8^\circ$ with the grid plane. Energies are plotted as functions of the applied field intensity B . The ground state energy is set equal to zero. Arrows indicate the anticrossings produced by S -mixing between the two lowest levels. The inset shows S_{eff} as functions of B for the same angle at $T = 0$, where S_{eff} is defined through the relation $S_{\text{eff}}(S_{\text{eff}} + 1) = \langle \mathbf{S}^2 \rangle$.

from J_{18} , J_{78} , J_{34} and J_{45} (see Fig. 1), whose values are 0.33 meV. Next-nearest-neighbor exchange interactions can be neglected. Concerning the local crystal-field, the second term in equation (1) can be approximately rewritten as

$$\sum_i \mathbf{s}_i \cdot \mathbf{D}_i \cdot \mathbf{s}_i = D \sum_i \left[s_{iz}^2 - \frac{1}{3} s_i(s_i + 1) \right], \quad (2)$$

with $D = -6.1 \mu\text{eV}$. The intracluster dipole-dipole interaction \mathbf{D}_{ij} has been evaluated within the point-dipole approximation [13]. At last, $g_i = 2$ is assumed, as appropriate for Mn(II) ions.

With these experimentally determined parameters, the energy spectrum for $\mathbf{B} = 0$ consists of many level multiplets with an almost definite value of S . The ground multiplet has $S = 5/2$, and the four lowest-lying excited multiplets have (in order of increasing energy) $S = 7/2$, $S = 3/2$, $S = 3/2$, $S = 9/2$. These multiplets are separated by the isotropic exchange and split by the anisotropic interactions. The lowest levels are shown in Figure 2. The application of a magnetic field \mathbf{B} in a direction outside the grid plane and different from that of the C_2 axis produces several ACs involving levels belonging to different multiplets (see Fig. 2). As the AC fields \mathbf{B}_c are approached the multiplet mixing is enhanced. For $\mathbf{B} = \mathbf{B}_c$, the spins in each cluster oscillate coherently between states with different values of S , which therefore is no longer a good quantum number. This can be inferred for example for the ground state ACs (indicated by the arrows in Fig. 2) from the inset in Figure 2, which shows the field-dependence at

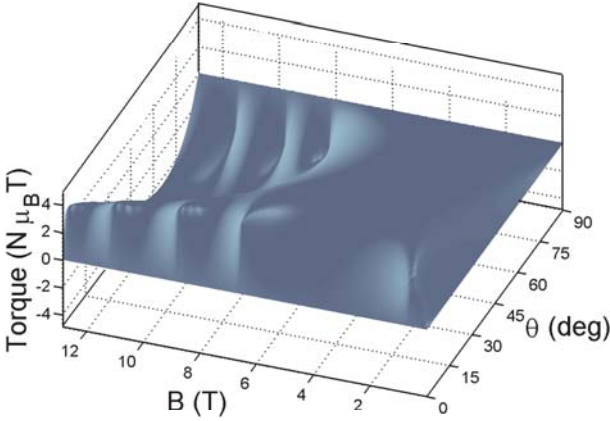


Fig. 3. Two-dimensional plot of the calculated torque as a function of the applied field direction θ and intensity B at $T = 0.05$ K with parameters of Hamiltonian equation (1) as given in the text.

$T = 0$ of the quantity S_{eff} , defined through the relation $S_{eff}(S_{eff} + 1) = \langle \mathbf{S}^2 \rangle$. When \mathbf{B} is close to \mathbf{B}_c the value of S_{eff} is intermediate between half integers, e.g. $5/2$ and $7/2$ at the first level AC, thus confirming that the ground-state wavefunction is a superposition of different total-spin states.

This opens a scenario in which not only the direction of the total spin fluctuates in time, as in the case of the well-studied quantum tunnelling of the magnetization [4–6], but even its length fluctuates (quantum dynamics of the total spin, or briefly QDTS). Moreover, by properly tuning the direction of the applied magnetic field, the AC splitting can be made as large as several kelvin degrees, thus overcoming the problem of decoherence due to hyperfine fields and to cluster-cluster interactions. Most importantly, in the Mn-[3×3] grid several of these ACs involve the two lowest energy levels, thus opening the possibility to detect the QDTS by means of *macroscopic* low-temperature magnetic bulk techniques. In particular, our calculations show that at low temperature, in correspondence to each AC between the two lowest lying states, a sharp peak should be detected in the torque signal (as function of the field intensity B) when the direction of the field θ is close to the grid plane ($\theta \cong 0^\circ$) or almost perpendicular to it ($\theta \cong 90^\circ$) (see Figs. 3 and 4). Such peaks are sharper the lower the temperature, but are still clearly visible at temperatures easily reachable experimentally. The precipitous drop of the torque signal as a function of θ near $\theta = 0^\circ$ and $\theta = 90^\circ$ is due to a change of sign imposed by symmetry (as $\mathbf{M} \times \mathbf{B} = 0$ when \mathbf{B} points along a principal direction of the susceptibility tensor of the system).

By comparing Figures 3 and 4 with the corresponding spectrum reported in Figure 2, it is evident that a torque peak appears in correspondence to each AC involving the ground state. While the first peak at low field corresponds to an intra-multiplet AC, the peaks at about 6.6, 8.9 and 11.2 tesla represent a direct consequence of the coherent superposition of different total spin quantum states. The link between the peaks in the torque signal

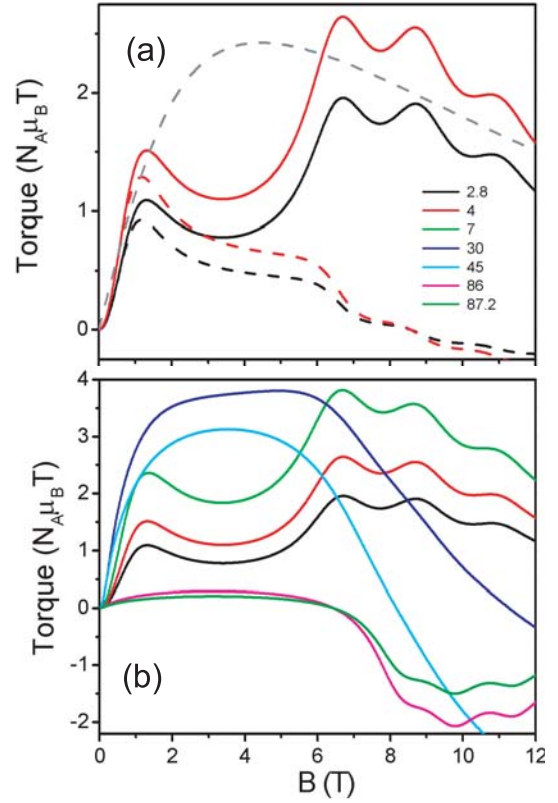


Fig. 4. (a) Plots of the calculated torque at $T = 0.4$ K as a function of the applied magnetic field B for two selected directions θ lying close to the grid plane. Colored dashed lines represent the calculated torque at the same angles with S -mixing eliminated by hand, i.e. with quantum fluctuations of $|\mathbf{S}|$ removed. The dashed gray line represents the torque calculated using the classical version of the Hamiltonian equation (1) at $T = 0$ for $\theta = 2.8^\circ$. The classical value of the torque has been rescaled (by 0.25) to fit the figure. (b) calculated torque at $T = 0.4$ K as a function of the applied field intensity B for several directions θ .

and the level ACs is demonstrated in Figure 4a, where the torque curves calculated with the mixing artificially forced to zero are shown by colored dashed lines. When S -mixing is neglected, every inter-multiplet AC becomes a crossing, the fluctuations of the total spin vector are suppressed and the peaks in the torque curve disappear. Thus, without S -mixing the torque curve should exhibit the step-like field dependence usually observed in MNMs [19]. The comparison between solid and dashed curves in Figure 4a shows clearly that the predicted peaks in the torque would be a direct macroscopic manifestation of the QDTS at the level ACs. Also, these spin fluctuations and the associated peaks are of purely quantum origin, as these are absent in the classical version of the Hamiltonian equation (1) (see the gray dashed curve in Fig. 4a).

The fact that these torque peaks directly reflect the large enhancement of quantum fluctuations of $|\mathbf{S}|$ at the ACs can be understood by a simple physical picture. In the following we define the z' axis parallel to \mathbf{B} . The torque is proportional to the magnetic response perpendicular to

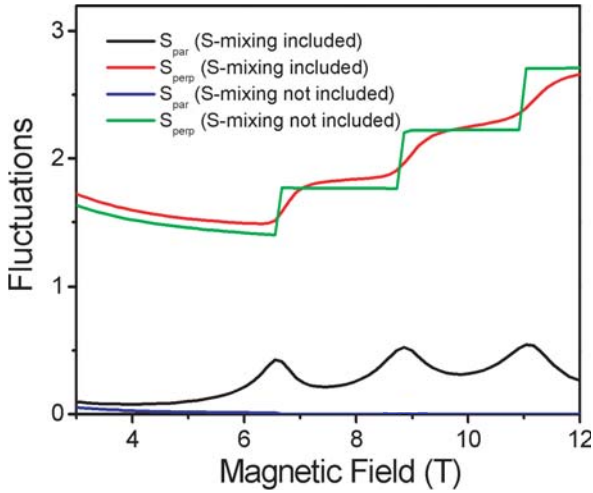


Fig. 5. Numerical calculations of the $T = 0$ fluctuations of $S_{z'}$ (“parallel”) and of $S_{x'}$ (“perpendicular”), as a function of the applied magnetic field (forming an angle $\theta = 2.8^\circ$ with the grid plane), with and without S -mixing. Parameters are given in the text.

the field direction, i.e. to $\langle S_{x'} \rangle$. Fluctuations of $|\mathbf{S}|$ are accompanied by fluctuations of the magnetization ($S_{z'}$) [20], and these latter are deeply connected with $\langle S_{x'} \rangle$. Accordingly, $S_{x'}$ tracks the increase and decrease of these fluctuations while sweeping over the AC, leading to a peak in the torque. Indeed, near the ACs, the ground-state wavefunction can be written to a good degree of approximation as

$$|G\rangle = \frac{1}{\sqrt{2}}(a(B)|\Gamma_1, M\rangle + b(B)|\Gamma_2, M+1\rangle), \quad (3)$$

where $a(B)^2 + b(B)^2 = 2$ by normalization. For $B \ll B_c$, $b(B) \sim 0$, $a(B) \sim \sqrt{2}$, and the ground state reduces approximately to an eigenstate of $S_{z'}$, $|\Gamma_1, M\rangle$, where M is the corresponding eigenvalue and Γ_1 represents the set of additional labels necessary to identify the state. For $B \gg B_c$, $a(B) \sim 0$, $b(B) \sim \sqrt{2}$, and the ground state reduces approximately to $|\Gamma_2, M+1\rangle$.

At $T = 0$ the torque is given by

$$\tau \propto B \langle S_{x'} \rangle = Ba(B)b(B) \langle \Gamma_1, M | S_{x'} | \Gamma_2, M+1 \rangle. \quad (4)$$

Since $\langle \Gamma_1, M | S_{x'} | \Gamma_2, M+1 \rangle$ is almost independent on B , the field dependence of τ comes entirely from the factor $Ba(B)b(B) = Bb(B)\sqrt{2-b(B)^2}$.

Quantum fluctuations of the magnetization are usually characterized by the quantity

$$(\Delta S_{z'})^2 = \langle S_{z'}^2 \rangle - \langle S_{z'} \rangle^2 = \frac{b(B)^2}{2} - \frac{b(B)^4}{4}. \quad (5)$$

Therefore,

$$\tau \propto 2B\Delta S_{z'}. \quad (6)$$

In case of anticrossing, $\Delta S_{z'}$ is maximum at B_c , where $b(B_c) = a(B_c) = 1$, and the torque peaks. In case of

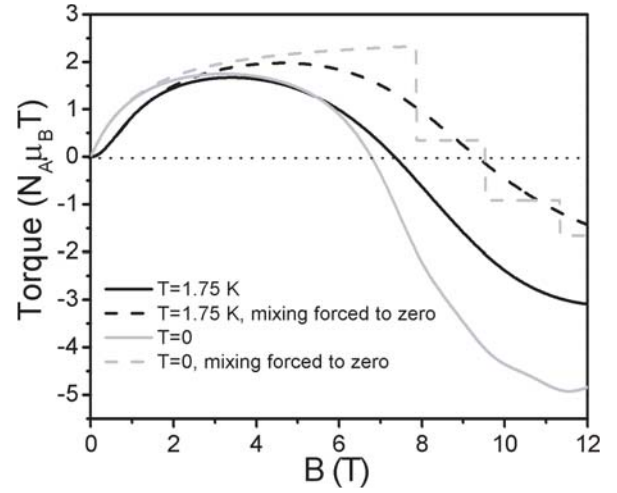


Fig. 6. Torque signal calculated for Mn-[3×3] at $T = 0$ and $T = 1.75$ K as a function of the amplitude of a magnetic field B applied along a direction forming an angle $\theta = 65.9^\circ$ with the grid plane. Dashed lines represent the calculated torque at the same angle and temperatures with S -mixing neglected.

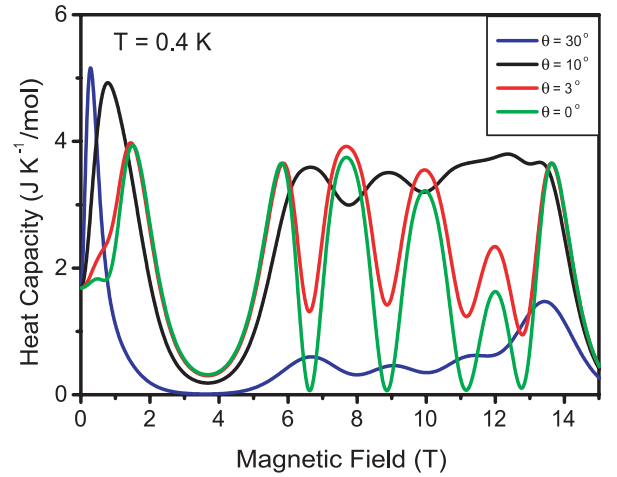


Fig. 7. Numerical calculations of the heat capacity as a function of the applied magnetic field for several directions θ , at $T = 0.4$ K.

crossing $\Delta S_{z'}$ is always zero because either $b(B) = 0$ or $a(B) = 0$, and the torque does not peak. As a further confirmation of this picture we show in Figure 5 numerical calculations of the fluctuations of $S_{z'}$ (“parallel”) and of $S_{x'}$ (“perpendicular”), with and without S -mixing.

The torque is the macroscopic magnetic bulk technique displaying the clearest signature of S -mixing. When the temperature T increases these effects wash out, and indeed published torque measurements on Mn-[3×3] [9] do not display peaks because data were collected at too high a temperature. Nevertheless, these measurements show another remarkable effect of S -mixing: a change of sign had been observed in the torque signal at $T = 1.75$ K and $B = 7.5$ T and this had been explained by assuming that the axial anisotropy was easy-axis for $S = 5/2$ and

easy-plane for $S = 7/2$. If S -mixing is neglected, the axial parameters describing the anisotropic splitting of the spin multiplets can be obtained by projecting the complete Hamiltonian onto each total-spin subspace (strong-exchange limit):

$$H_{sub} = D_{sub} \left[S_z^2 - \frac{1}{3}S(S+1) \right], \quad (7)$$

where \mathbf{S} is a vector spin operator with S equal to the total spin of the subspace.

The parameter D_{sub} is determined by crystal field and dipolar projection coefficients. We find for the two lowest multiplets

$$D_{5/2} = -41 \mu\text{eV}, D_{7/2} = -2.5 \mu\text{eV}. \quad (8)$$

The origin of the change of sign is therefore different from that proposed in [9]. Indeed, this effect comes from the interplay of the positive value of the axial anisotropy for the higher-lying $S = 9/2$ level ($D_{9/2} = 3.8 \mu\text{eV}$) on the one hand, and S -mixing on the other hand. In the lack of S -mixing the change of sign in the torque would occur at about 9 T, when a state belonging to the $S = 9/2$ manifold becomes the ground state. However, since the $S = 7/2$ and $S = 9/2$ multiplets mix heavily, the change of sign is shifted to lower fields (see Fig. 6).

We have also calculated the low- T heat capacity as a function of the applied field (see Fig. 7). This quantity provides a way to assess the value of the AC gaps as a function of the field direction. For $\theta \neq 0$ anticrossings open up and the heat capacity does not vanish at B_c .

In this paper we have identified a new clear-cut macroscopic manifestation of a quantum phenomenon characterizing the microscopic dynamics of magnetic clusters. We have shown that torque measurements can provide direct evidence of quantum fluctuations of the total spin length, and we have studied a model system displaying such effect. The comprehensive understanding of the spin dynamics in mesoscopic systems like molecular nanomagnets is essential to understand the crossover between quantum and classical mechanics and to make rational design of these compounds possible, especially in view of the promising applications.

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