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

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Received 9 October 2003
Published online 8 December 2003 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2003

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.

PACS. 75.45.+j Macroscopic quantum phenomena in magnetic systems – 75.50.Xx Molecular magnets – 52.70.Ds Electric and magnetic measurements

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 macroscopic 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]

\[
H = \sum_{i>j} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j + \sum_i s_i \cdot \mathbf{D}_i \cdot \mathbf{s}_i + \sum_{i>j} s_i \cdot \mathbf{D}_{ij} \cdot s_j + \mu_B \sum_i g_i \mathbf{B} \cdot \mathbf{s}_i, \tag{1}
\]

where \( s_i \) 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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In this paper we show that favorable conditions are met in the Mn(II)-[3×3] grid-like cluster [Mn$_9$(2POAP-2H)$_6$](ClO$_4$)$_6$·3.57MeCN·H$_2$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 the exchange part of the spin Hamiltonian belonging 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 $|S\rangle$ 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 $|S\rangle$ 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 [Mn$_9$(2POAP-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 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

$$\sum_i s_i \cdot D_{ij} \cdot s_j = D \sum_i \left[ s_i^2 - \frac{1}{3} s_i (s_i + 1) \right],$$

with $D = -6.1 \, \text{μeV}$. The intracluster dipole-dipole interaction $D_{ij}$ 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 $B = 0$ 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 $B$ 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 $B_{ac}$ are approached the multiplet mixing is enhanced. For $B = B_{ac}$, 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