Influence of the Dzyaloshinskii-Moriya Exchange Interaction on Quantum Phase Interference of Spins

W. Wernsdorfer,[1] T. C. Stamatatos,[2] and G. Christou[2]
[1]Institut Néel, CNRS and Université J. Fourier, BP 166, 38042 Grenoble Cedex 9, France
[2]Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, USA
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Magnetization measurements of a Mn_{12}mda wheel single-molecule magnet with a spin ground state of $S = 7$ show resonant tunneling and quantum phase interference, which are established by studying the tunnel rates as a function of a transverse field applied along the hard magnetization axis. A Dzyaloshinskii-Moriya (DM) exchange interaction allows the tunneling between different spin multiplets. It is shown that the quantum phase interference of these transitions is strongly dependent on the direction of the DM vector.

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Single-molecule magnets (SMMs), sometimes called molecular nanomagnets, consist of an inner magnetic core and a surrounding shell of organic ligands [1] that can be tailored to bind onto surfaces or into junctions. SMMs come in a variety of shapes and sizes and permit selective substitution of the ligands in order to alter the coupling to the environment. It is also possible to exchange the magnetic ions, thus changing the magnetic properties without modifying the structure and the coupling to the environment. SMMs combine the classic macroscale properties of a magnet with the quantum properties of a nanoscale entity. They display an impressive array of quantum effects that are observable up to higher and higher temperatures due to progress in molecular design, ranging from quantum tunnelling of magnetization [2–4] to Berry phase interference [5–8] and quantum coherence [9,10] with important consequences on the physics of spintronic devices [11].

Up to now, the spin system of an SMM has mainly been described by a single spin S, and the associated tunneling processes were transitions inside the multiplet of S [1]. Recent studies in the field of molecular magnetism go beyond this giant-spin approximation, describing the molecule as a multispin system [12]. In this case, the total spin S of the molecule is not fixed, but several multiplets with different total spins appear and the number of allowed tunnel transitions and relaxation paths of the spin system increase considerably. For a simple multispin description with symmetric exchange coupling between spins, tunneling between different multiplets is forbidden. However, antisymmetric exchange coupling between spins, that is the Dzyaloshinskii-Moriya (DM) interaction, can lift the degeneracy of energy level crossings belonging to different spin multiplets, and tunneling and interference between these levels become allowed [12–14]. DM interactions result in general from pairwise interactions of neighboring spins that do not have an inversion center. This condition is fullfilled most of the time in SMMs even when the entire molecule has an inversion center [14,15].

We present here resonant quantum tunneling measurements of a Mn_{12}mda wheel [16], which is a member of the $[Mn_{12}(O_2CMe)_{14}(R\text{-mda})_8]$ family of loops, all with the same core and metal topologies but with R-substituted mda^{2-} groups [17]. We show that this compound exhibits quantum phase interference effects at all observed tunnel resonances and that the phase of interference depends strongly on the direction of the DM vector $\vec{D}_{1,2}$.

The Mn_{12}mda ($R = Me$) wheel was prepared by the reaction of $Mn(O_2CMe)_2 4H_2O$ and N-methyldiethanolamine ($mdaH_2$) in the presence of the organic base NEt_3, and crystallizes as dark red platelike crystals in triclinic space group $P\bar{1}$. Full details of the synthesis, crystal structure, and magnetic characterization were presented elsewhere [16], establishing a ground state spin $S = 7$. The wheel consists of alternating Mn^{2+} and Mn^{3+} ions, and therefore all subunits consisting of two neighboring Mn ions must lack an inversion center, justifying therefore the possibility of DM interactions even though the complete molecule has an inversion center [14,15]. Although our Mn_{12}mda wheel is very similar to those in [13,17], the hysteresis loops show resonant tunneling steps that are much more narrow, allowing us to study in detail the quantum effects involved.

The magnetization measurements were performed by using a micro-SQUID setup [18] on top of which a single crystal of Mn_{12}mda wheels was placed. The field was aligned with the easy axis of magnetization using the transverse field method [19].

Figure 1(a) shows the temperature dependence of the hysteresis loops of Mn_{12}mda wheels. The loops display a series of steps, separated by plateaus. As the temperature is lowered, the hysteresis increases because there is a decrease in the transition rate of thermally assisted tunneling [2,3]. The hysteresis loops become temperature independent below 0.3 K, demonstrating quantum tunneling at the lowest energy levels [4]. Apart from the major steps, these hysteresis loops reveal fine structure in the thermally activated regime. In order to determine precisely the resonance

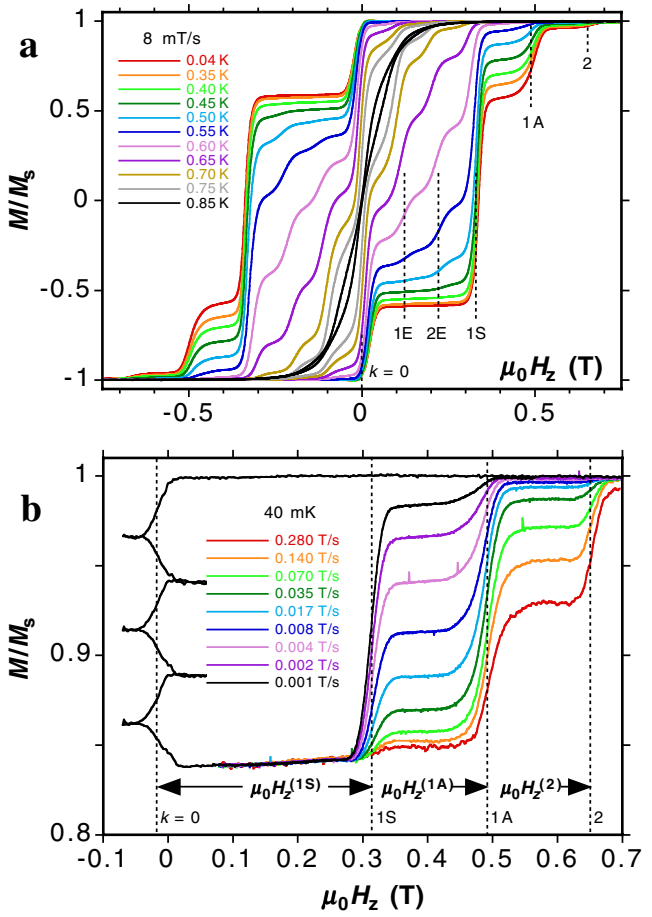

FIG. 1 (color online). (a) Hysteresis loops of single crystals of Mn_{12}mda wheels at different temperatures and a constant field sweep rate of 8 mT/s. (b) Minor hysteresis loops at 0.04 K. The magnetization was first saturated at 1 T. After ramping the field to zero at 0.14 T/s, the field was swept 3 times back and forth (between ± 0.07 T) over the zero-field resonance $k = 0$ with a sweep rate of 0.28 T/s. Then, the field is quickly swept back to 1 T at the indicated field sweep rates leading to resonant tunneling at the transitions $k = 1S$, $1A$, and 2. The corresponding field values are used to find the spin Hamiltonian parameters D and J.

positions, we used the minor loop method described in [20]. A typical example is presented in Fig. 1(b).

In order to explain the observed tunnel resonances and tunnel probabilities, and to study the influence of DM interaction on quantum phase interference, we model the 12-spin-system with a simple dimer model of two ferromagnetically coupled spins $S_1 = S_2 = 7/2$ [13,16]. Although this model can be questioned [14,21], it represents a useful simplification that keeps the required calculations manageable, has been found to describe well the lowest energy levels, and allows a qualitative discussion of the observed tunnel rates. The simple model employed does not affect the generality of the obtained conclusions about the influence of the DM interaction to be described. Each spin S_i is described by the spin Hamiltonian:

$$\mathcal{H}_i = -DS_{i,z}^2 + E(S_{i,x}^2 - S_{i,y}^2) + \hat{O}(4) - g\mu_B\mu_0\vec{S}_i \cdot \vec{H}, \quad (1)$$

$S_{i,x}$, $S_{i,y}$, and $S_{i,z}$ are the vector components of the ith spin operator and $g \approx 2$. The first two terms describe the uniaxial anisotropy of the molecule, with longitudinal and transverse anisotropy parameters D and E. The third term contains higher order crystal field anisotropy terms. The last term is the Zeeman interaction of the spin $\vec{S}_i$ with an external magnetic field $\vec{H}$.

The exchange interaction between the two spins can be described by

$$\mathcal{H}_{\text{ex}} = J\vec{S}_1 \cdot \vec{S}_2 + \vec{D}_{1,2} \cdot (\vec{S}_1 \times \vec{S}_2), \quad (2)$$

where the first term describes the isotropic Heisenberg exchange interaction with exchange constant J, the second term is an antisymmetric DM interaction between the two spins, and $\vec{D}_{1,2}$ is the DM vector.

Exact diagonalization of the total spin Hamiltonian $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{ex}}$ and use of $J = -0.435$ K and $D = 0.985$ K lead to the energy spectrum shown in Fig. 2. The lowest lying spin states belong to the $S = 7$ and $S = 6$ multiplets. Because of the ferromagnetic exchange, the first excited spin multiplet's $|S = 6, M_S = \pm 6\rangle$ doublet is located at about 8.8 K above the ground state doublet $|S = 7, M_S = \pm 7\rangle$ in zero magnetic field. Using $D = 0.985$ K and $J = -0.435$ K, we can reproduce well the 6 observed tunnel transitions. The resonances $k = 0$, $1S$, and 2 correspond to transitions between the states of the $S = 7$ multiplet, whereas $k = 1A$, $1E$, and $2E$ correspond to transitions between the $S = 7$ and $S = 6$ multiplets. The latter ones are not allowed unless the antisymmetric DM interaction between the two spins is introduced [Eq. (2)].

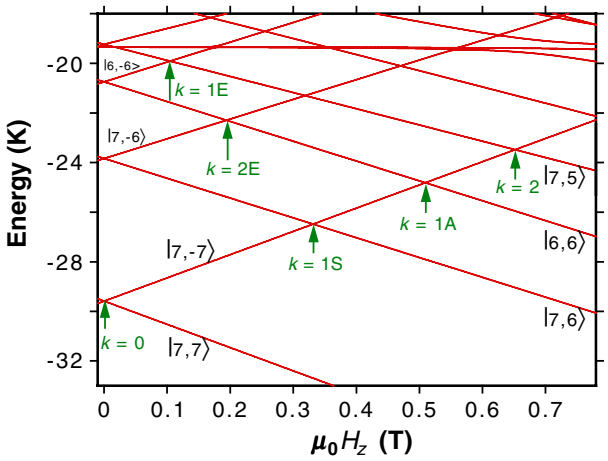

FIG. 2 (color online). Zeeman diagram of the lowest energy levels used to explain the observed resonance tunnel transitions in Fig. 1. The field H_z is along the easy axis of magnetization. The levels are labeled with quantum numbers $|S, M_S\rangle$ and the observed level crossings are indicated with k.

In order to get more insight into the tunnel process, we studied the tunnel resonances as a function of a transverse field and used the Landau-Zener (LZ) method [6,22,23]. We first placed a crystal of the Mn_{12}mda wheel in a high negative field H_z to saturate the magnetization at 40 mK. We then swept the applied field at a constant rate dH_z/dt over the $k = 0$ resonance transition and measured the variation of magnetization using a micro-SQUID. For the other transitions, we used the minor loop method [20] [Fig. 1(b)]. The fraction of molecules that reversed their spin was deduced from the step height, giving the LZ tunnel probability P_k between two quantum states m and m'. We deduced the corresponding tunnel splitting Δ_k using the LZ equation:

$$P_k = 1 - \exp\left[-\frac{\pi\Delta_k^2}{2\hbar g\mu_B|m - m'|\mu_0 dH_z/dt}\right]. \quad (3)$$

Its validity can be tested by plotting Δ_k as a function of dH_z/dt [22,23]. We found that the LZ method is only applicable in the region of high sweep rates where Δ_k is independent of the field sweep rate. For the $k = 0$ resonance, this region is achieved for about $\mu_0 dH_z/dt > 0.1$ T/s. The deviations from the LZ equation at lower sweep rates have been studied in detail [23,24] and are mainly due to reshuffling of internal fields [25]. Note that Δ_k obtained at lower sweep rates always underestimates the real Δ_k, it can therefore be used only as a lower-limit estimation [14].

Figure 3 shows Δ_k as a function of a transverse field H_{tr}, applied approximately along the hard axis of magnetization (x axis) and measured at $\mu_0 dH_z/dt = 0.56$ T/s. The observed oscillations can be explained by quantum phase interference of two tunnel paths [5] and has been observed in other SMMs [6–8,13,14]. We used the period of oscillation to determine the transverse anisotropy parameter $E = 0.19$ K [Eq. (1)]. At $\mu_0 dH_z/dt = 0.56$ T/s, the LZ method is applicable only for $k = 0$ and approximatively for $k = 1$ S. However, for $k = 1$ A the sweep rate was too slow to apply the LZ method and we therefore plot only the tunnel probability in Fig. 3(c).

Figures 3(d) and 3(e) shows the tunnel probabilities for excited state tunnel transitions $k = 1E$ and $2E$. Here, phonons first excite the spin from the ground state $|S, M_S\rangle = |7, -7\rangle$ to the first or second excited spin states $|7, -6\rangle$ or $|6, -6\rangle$. Then, during the LZ field sweep, the spin tunnels to $|6, 6\rangle$ or $|7, 5\rangle$, respectively. Although this method can yield the activation energies and level lifetimes [23], the tunnel splittings are difficult to deduce. Nevertheless, the tunnel probabilities P_k can be found and studied as a function of transverse field [Figs. 3(d) and 3(e)], showing clearly oscillations of P_k.

In multispin systems, transitions between different multiplets can be allowed by DM interactions, that is, the observation of tunneling at $k = 1E$, $2E$, and $1A$ establishes the presence of a DM interaction in Mn_{12}mda wheels. A very interesting observation is that the oscillations of the tunnel probabilities are not symmetrical with respect to the sign of the transverse field ($P_k(H_{tr}) \neq P_k(-H_{tr})$). This is in clear contrast to transitions between states of the same multiplet [$k = 0$ and $1S$, see Figs. 3(a) and 3(b)]. Numerical diagonalization of the total spin Hamiltonian $\mathcal{H}$ shows that the phase of the oscillation depends strongly on the orientation of the DM vector $\vec{D}_{1,2}$ [Eq. (2)]. Expressing $\vec{D}_{1,2}$ in terms of the modulus $|\vec{D}_{1,2}|$ and the usual polar angles θ_{DM} and φ_{DM} defined with respect to the z axis, we found that (i) for small values of $|\vec{D}_{1,2}|$, Δ_k does not depend on DM interaction for a transition within a spin multiplet, and (ii) Δ_k depends strongly on $|\vec{D}_{1,2}|$ and θ_{DM} for a transition between spin multiplets, whereas it hardly depends on φ_{DM}. Δ_k is nearly proportional to $|\vec{D}_{1,2}|$ and the period of oscillation is close to those for transitions within a spin multiplet. Figures 4 and 5 show a few examples of Δ_k calculated with the Hamiltonian parameters given above, $|\vec{D}_{1,2}| = 0.03$ K, and several θ_{DM} values. We find the best agreement for $\theta_{DM} \approx 10°$.

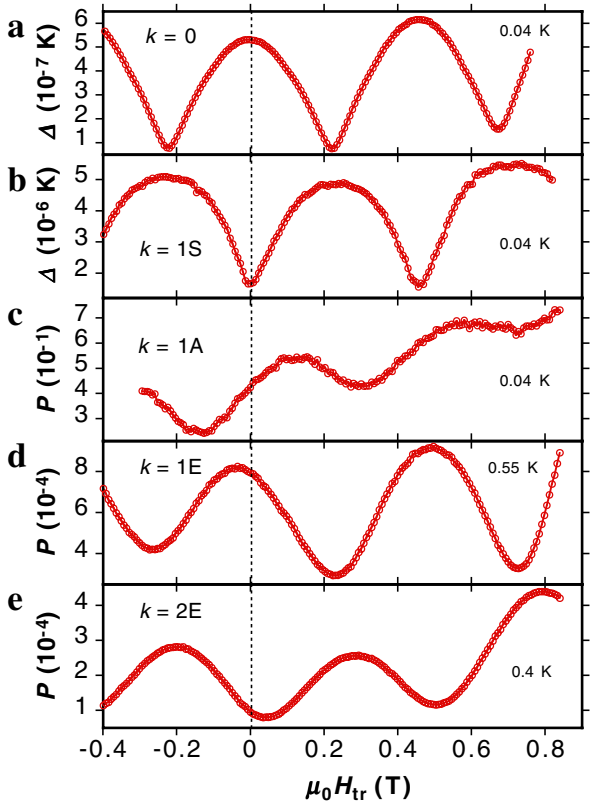

FIG. 3 (color online). Transverse field H_{tr} dependence of the tunnel splitting (a)–(b) and the tunnel probability (c)–(e) for the indicated tunnel transitions. H_{tr} was corrected by a mean internal transverse field of about 10 mT, which was determined by measurements performed at positive and negative magnetization of the crystal.

We would like to point out two deviations between the measurements and the dimer model, which we believe are due to the approximate nature of the latter. First, the experimental values of Δ_k for $k = 0$ and 1 S are about

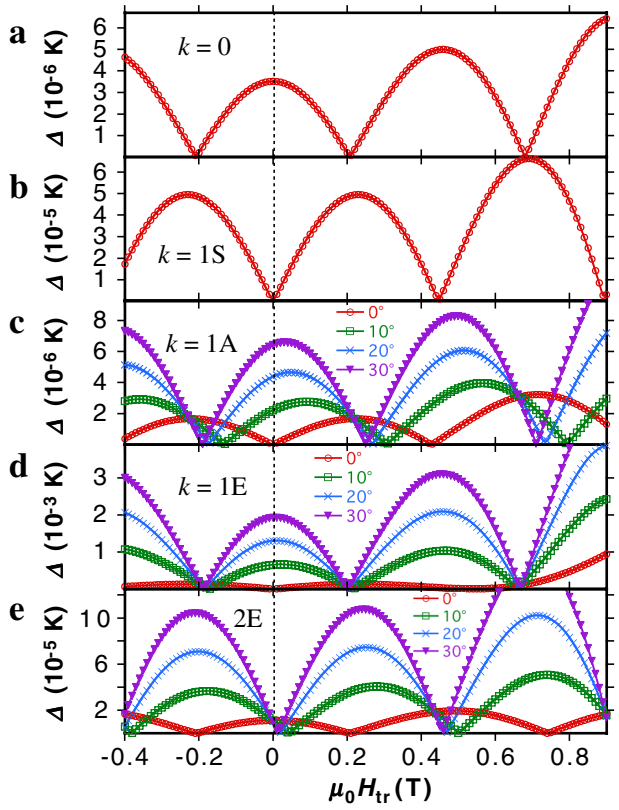

FIG. 4 (color online). Calculated tunnel splitting for the indicated tunnel transitions k as a function of transverse field. θ_{DM} is indicated in (c)–(e) showing that the phases of the oscillations depend strongly on θ_{DM}. The best agreement with the data in Figs. 3(c)–3(e) is achieved for $\theta_{\mathrm{DM}} = 10°$.

1 order of magnitude smaller than the calculated ones. This discrepancy, also observed for a similar molecule [13,14], can be reduced by introducing $\hat{O}(4)$ terms but it seems impossible to reproduce simultaneously the periods of oscillation and the values of Δ_k. Second, the tunnel rates

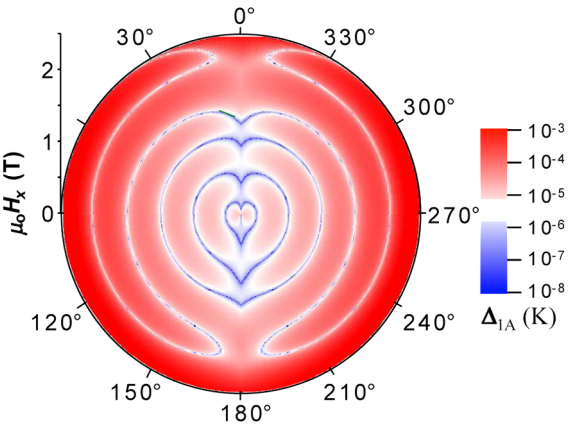

FIG. 5 (color online). Color-scale representation of the calculated tunnel splitting for the tunnel transitions $k = 1A$ as a function of transverse field H_z and the angle θ_{DM} of the DM vector $\vec{D}_{1,2}$.

for $k = 1E$, $2E$, and $1A$ can be adjusted with the values of $|\vec{D}_{1,2}|$ and the phase of oscillation with θ_{DM}. However, we did not manage to find a θ_{DM} value that fits simultaneously the phases of all three transitions. These deviations should motivate more theoretical work on the subject, as well as extensions to more sophisticated models for the Mn_{12} wheel involving two sets of six independent Mn spins.

In conclusion, we have shown for the first time how the DM interactions can affect the tunneling transitions and quantum phase interference of a SMM. Of particular novelty and importance is the phase shift observed in the tunnel probabilities of some transitions as a function of the DM vector orientation. Such observations are of importance to potential applications of SMMs that hope to take advantage of the tunneling processes that such molecules can undergo.

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