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Quantum Phase Interference and Spin-Parity in Mn$_{12}$ Single-Molecule Magnets

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Magnetization measurements of Mn$_{12}$ molecular nanomagnets with spin ground states of $S = 10$ and $S = 19/2$ show resonance tunneling at avoided energy level crossings. The observed oscillations of the tunnel probability as a function of the magnetic field applied along the hard anisotropy axis are due to topological quantum phase interference of two tunnel paths of opposite windings. Spin-parity dependent tunneling is established by comparing the quantum phase interference of integer and half-integer spin systems.

Single-molecule magnets (SMMs) are among the most promising candidates to observe the limits between classical and quantum physics since they have a well defined structure, spin ground state, and magnetic anisotropy. The first SMM was Mn$_{12}$acetate [1]. It exhibits slow magnetization relaxation of its $S = 10$ ground state which is split by axial zero-field splitting. It was the first system to show thermally assisted tunneling of magnetization [2,3], and Fe$_8$ and Mn$_4$ SMMs were the first to exhibit ground state tunneling [4,5]. Tunneling was also found in other SMMs (see, for instance, [6–8]).

Quantum phase interference [9] and spin-parity effects are among the most interesting quantum phenomena that can be studied at the mesoscopic level in SMMs. The former was recently observed in Fe$_8$ and $[\text{Mn}_{12}]^{2-}$ SMMs [10,11] and has led to many new theoretical studies on this effect in spin systems [12–21]. The latter predicts that quantum tunneling is suppressed at zero applied field if the total spin of the magnetic system is half-integer but is allowed in integer spin systems. Enz, Schilling, Van Hemmen, and Süto [22,23] were the first to suggest the absence of tunneling as a consequence of Kramers degeneracy [24]. It was then shown that tunneling can even be absent without Kramers degeneracy [9,25,26], i.e., quantum phase interference can lead to destructive interference and thus suppression of tunneling.

There are several reasons why quantum phase interference [10,11] and spin-parity effects [27] are difficult to observe. The main one is the influence of environmental degrees of freedom that can induce or suppress tunneling: hyperfine and dipolar couplings can induce tunneling via transverse field components, intermolecular exchange coupling may enhance or suppress tunneling depending on its strength, phonons can induce transitions via excited states, and faster-relaxing species can complicate the interpretation [28].

We present here the first half-integer spin SMM that clearly shows quantum phase interference and spin-parity effects. The syntheses, crystal structures, and magnetic

properties of the studied complexes are reported elsewhere [29]. The compounds are $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{F}_5)_{16}(\text{H}_2\text{O})_4]$, $(\text{NMe}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{F}_5)_{16}(\text{H}_2\text{O})_4]$, and $(\text{NMe}_4)_2[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{F}_5)_{16}(\text{H}_2\text{O})_4]$ (called Mn$_{12}$, $[\text{Mn}_{12}]^-$, and $[\text{Mn}_{12}]^{2-}$, respectively). Reaction of Mn$_{12}$ with one and two equivalents of NMe$_4$I affords the one- and two-electron reduced analogs, $[\text{Mn}_{12}]^-$ and $[\text{Mn}_{12}]^{2-}$, respectively. The three complexes crystallize in the triclinic $P1$ bar, monoclinic $P2/c$, and monoclinic $C2/c$ space groups, respectively, with all molecules in the crystals aligned with their z axes parallel. This crystallographic finding has been confirmed using the transverse-field method [30]. The molecular structures are all very similar, each consisting of a central $[\text{Mn}^{IV}\text{O}_4]$ cubane core that is surrounded by a nonplanar ring of eight Mn^{III} ions. Bond valence sum calculations establish that the added electrons in $[\text{Mn}_{12}]^-$ and $[\text{Mn}_{12}]^{2-}$ are localized on former Mn^{III} ions giving trapped-valence Mn$_4^{IV}$Mn$_7^{III}$Mn^{II} and Mn$_4^{IV}$Mn$_6^{III}$Mn$_2^{II}$ anions, respectively.

Magnetization studies yield $S = 10$, $D = 0.58$ K, $g = 1.87$ for Mn$_{12}$, $S = 19/2$, $D = 0.49$ K, $g = 2.04$, for $[\text{Mn}_{12}]^-$, and $S = 10$, $D = 0.42$ K, $g = 2.05$, for $[\text{Mn}_{12}]^{2-}$, where D is the axial zero-field splitting parameter [29]. AC susceptibility and relaxation measurements give Arrhenius plots from which were obtained the effective barriers to magnetization reversal: 59 K for Mn$_{12}$, 49 K for $[\text{Mn}_{12}]^-$, and 25 K for $[\text{Mn}_{12}]^{2-}$.

The simplest model describing the spin system of the three Mn$_{12}$ SMMs has the following Hamiltonian

$$H = -DS_z^2 + E(S_x^2 - S_y^2) - g\mu_B\mu_0\vec{S}\vec{H}. \quad (1)$$

S_x, S_y, and S_z are the three components of the spin operator, D and E are the anisotropy constants, and the last term describes the Zeeman energy associated with an applied field $\vec{H}$. This Hamiltonian defines hard, medium, and easy axes of magnetization in the x, y, and z directions, respectively, (Fig. 1). It has an energy level spectrum with ($2S + 1$) values which, to a first approximation, can be labeled by

the quantum numbers $m = -S, -(S - 1), \dots, S$ taking the z axis as the quantization axis. The energy spectrum can be obtained by using standard diagonalization techniques of the $[(2S + 1) \times (2S + 1)]$ matrix. At $\vec{H} = 0$, the levels $m = \pm S$ have the lowest energy. When a field H_z is applied, the levels with $m < 0$ increase in energy, while those with $m > 0$ decrease. Therefore, energy levels of positive and negative quantum numbers cross at certain values of H_z, given by $\mu_0 H_z \approx nD/g\mu_B$, with $n = 0, 1, 2, 3, \dots$.

When the spin Hamiltonian contains transverse terms (for instance $E(S_x^2 - S_y^2)$), the level crossings can be avoided level crossings. The spin S is in resonance between two states when the local longitudinal field is close to an avoided level crossing. The energy gap, the so-called tunnel splitting Δ, can be tuned by a transverse field (Fig. 1) via the $S_x H_x$ and $S_y H_y$ Zeeman terms. In the case of the transverse term $E(S_x^2 - S_y^2)$, it was shown that Δ oscillates with a period given by [9]

$$\mu_0 \Delta H = \frac{2k_B}{g\mu_B} \sqrt{2E(E + D)}. \qquad (2)$$

The oscillations are explained by constructive or destructive interference of quantum spin phases (Berry phases) of two tunnel paths [9] (Fig. 1).
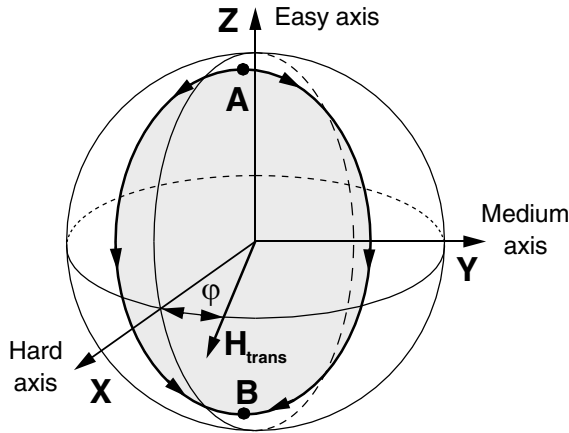

FIG. 1. Unit sphere showing degenerate minima **A** and **B** joined by two tunnel paths (heavy lines). The hard, medium, and easy axes are taken in the x, y, and z direction, respectively. The constant transverse field H_{trans} for tunnel splitting measurements is applied in the xy plane at an azimuth angle φ. At zero applied field $\vec{H} = 0$, the giant spin reversal results from the interference of two quantum spin paths of opposite direction in the easy anisotropy yz plane. For transverse fields in the direction of the hard axis, the two quantum spin paths are in a plane which is parallel to the yz plane, as indicated in the figure. It has been shown [9] that destructive interference—that is a quench of the tunneling rate—occurs whenever the shaded area is $k\pi/S$, where k is an odd integer. The interference effects disappear quickly when the transverse field has a component in the y direction because the tunneling is then dominated by only one quantum spin path.

All measurements were performed on single crystals using micro-SQUIDs [31]. The field can be applied in any direction by separately driving three orthogonal superconducting coils. The field was aligned using the transverse-field method [30].

Figure 2 shows typical hysteresis loop measurements on a single crystal of the three Mn_{12} samples. When the applied field is near an avoided level crossing, the magnetization relaxes faster, yielding steps separated by plateaus. As the temperature is lowered, there is a decrease in the
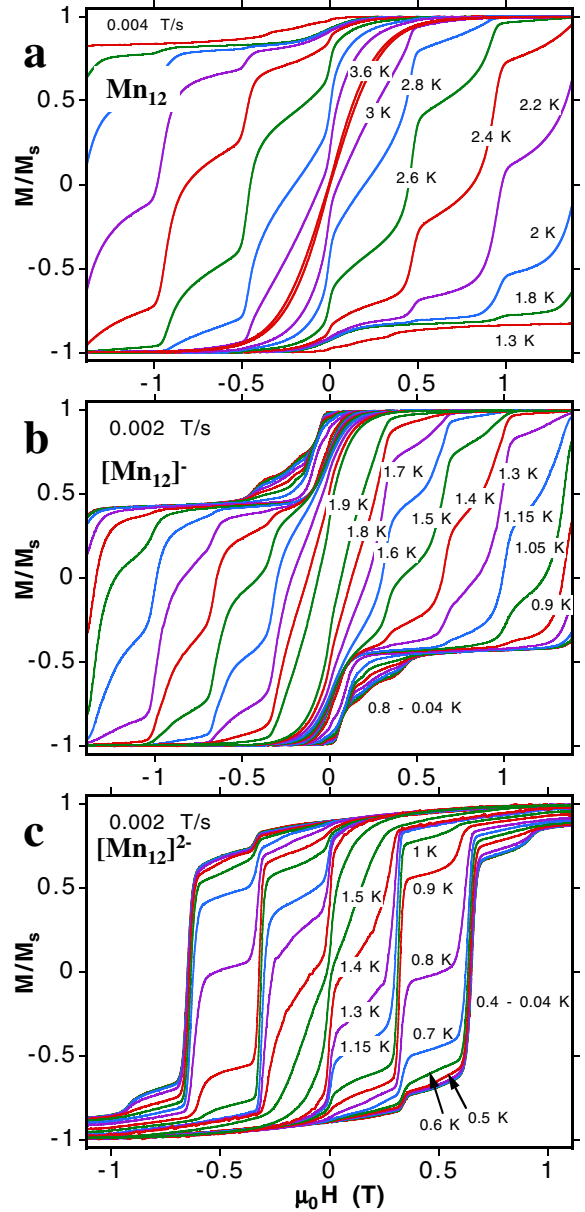

FIG. 2 (color online). Hysteresis loops of single crystals of (a) Mn_{12}, (b) $[Mn_{12}]^-$, and (c) $[Mn_{12}]^{2-}$ molecular clusters at different temperatures and a constant field sweep rate indicated in the figure. Note the large zero-field step of $[Mn_{12}]^-$ which is due to about 30% of fast-relaxing species [34].
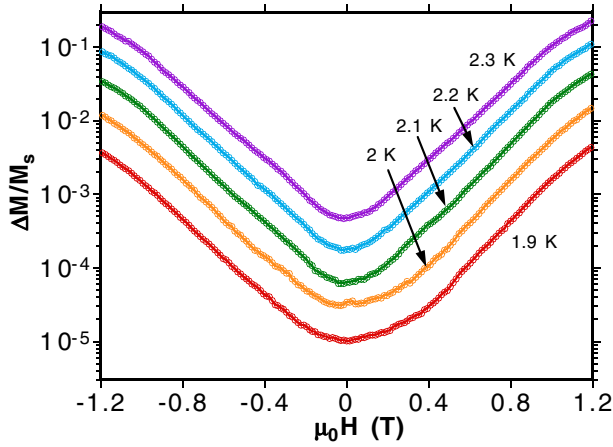
FIG. 3 (color online).   Transverse-field dependence of the fraction of Mn_{12} molecules which reversed their magnetization after the field was swept over the zero-field resonance at a rate of 0.28 T/s and at several temperatures.

FIG. 4 (color online).   Transverse-field dependence of the fraction of $[Mn_{12}]^-$ molecules which reversed their magnetization after the field was swept over the zero-field resonance at a rate of 0.28 T/s (a) at several temperatures and (b) at 1.7 K and two azimuth angles φ. The contribution of the fast-relaxing species is subtracted [34]. The observed oscillations are direct evidence for quantum phase interference. The minimum of the tunnel rate at zero transverse field is due to Kramers spin-parity.

transition rate as a result of reduced thermally assisted tunneling. Below about T_c = 0.65, 0.5, and 0.35 K, respectively, for Mn_{12}, $[Mn_{12}]^-$, and $[Mn_{12}]^{2-}$, the hysteresis loops become temperature independent, which suggests that ground state tunneling is dominating. The field between two resonances allows an estimation of the anisotropy constants D, and values of $D \approx 0.64$, 0.44, and 0.42 K were determined (supposing $g = 2$), respectively, for Mn_{12}, $[Mn_{12}]^-$, and $[Mn_{12}]^{2-}$, being in good agreement with other magnetization studies [29].

We have tried to use the Landau-Zener method [32,33] to measure the tunnel splitting as a function of transverse field as previously reported for Fe_8 [10]. However, the tunnel probability in the pure quantum regime (below T_c) was too small for our measuring technique [34] for Mn_{12} and $[Mn_{12}]^-$. We therefore studied the tunnel probability in the thermally activated regime [35].

In order to measure the tunnel probability, the crystals of Mn_{12} SMMs were first placed in a high negative field, yielding a saturated initial magnetization. Then, the applied field was swept at a constant rate of 0.28 T/s over the zero-field resonance transitions and the fraction of molecules which reversed their spin was measured. In the case of very small tunnel probabilities, the field was swept back and forth over the zero-field resonance until a larger fraction of molecules reversed their spin. A scaling procedure yields the probability of one sweep. This experiment was then repeated but in the presence of a constant transverse field. A typical result is presented in Fig. 3 for Mn_{12} showing a monotonic increase of the tunnel probability. Measurements at different azimuth angles φ (Fig. 1) did not show a significant difference. However, similar measurements on $[Mn_{12}]^-$ (Fig. 4) and $[Mn_{12}]^{2-}$ (Fig. 5) showed oscillations of the tunnel probability as a function of the magnetic field applied along the hard anisotropy axis $\varphi = 0°$ whereas no oscillations are observed for $\varphi = 90°$.

These oscillations are due to topological quantum interference of two tunnel paths of opposite windings [9]. The measurements of $[Mn_{12}]^{2-}$ are similar to the result on the Fe_8 molecular cluster [10,35]; however, those of $[Mn_{12}]^-$ show a minimum of the tunnel probability at zero transverse field. This is due to the spin-parity effect that predicts the absence of tunneling as a consequence of Kramers degeneracy [24]. The period of oscillation allows an estimation of the anisotropy constant E [see Eq. (2)] and values of $E \approx 0$, 0.047, and 0.086 K were obtained for Mn_{12}, $[Mn_{12}]^-$, and $[Mn_{12}]^{2-}$, respectively.

In conclusion, magnetization measurements of three molecular Mn_{12} clusters with a spin ground state of $S = 10$ and $S = 19/2$ show resonance tunneling at avoided energy level crossings. The observed oscillations of the tunnel probability as a function of a transverse field are due to topological quantum phase interference of two tunnel paths of opposite windings. Spin-parity dependent tunneling is established by comparing the quantum phase interference of integer and half-integer spin systems.
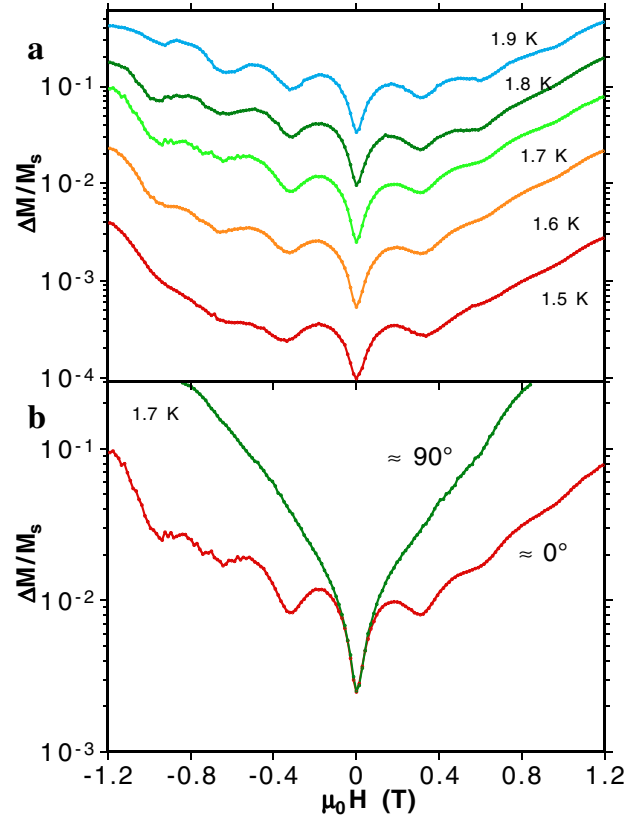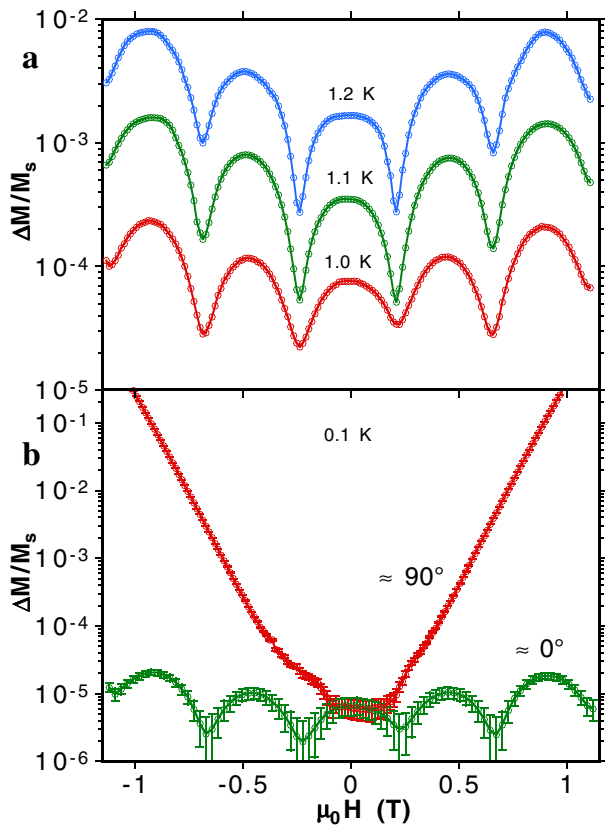
FIG. 5 (color online).   Transverse-field dependence of the fraction of $[Mn_{12}]^{2-}$ molecules which reversed their magnetization after the field was swept over the zero-field resonance at a rate of 0.28 T/s (a) at several temperatures and (b) at 0.1 K and two azimuth angles φ.

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