

Quantum phase interference (Berry phase) in single-molecule magnets of $[\text{Mn}_{12}]^{2-}$

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Magnetization measurements of molecular clusters $[\text{Mn}_{12}]^{2-}$ with a spin ground state of $S=10$ 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. $[\text{Mn}_{12}]^{2-}$ is therefore the second molecular cluster exhibiting quantum phase interference. © 2002 American Institute of Physics. [DOI: 10.1063/1.1450788]

Studying the limits between classical and quantum physics has become a very attractive field of research. Single-molecule magnets (SMMs) are among the most promising candidates in which to observe these phenomena since they have a well defined structure with well characterized spin ground state and magnetic anisotropy.^{1,2} Quantum phase interference³ is among the most interesting quantum phenomena that can be studied at the mesoscopic level in SMMs. This effect was recently observed in the Fe_8 SMM.⁴ It has led to new theoretical studies on quantum phase interference in spin systems.⁵⁻²² We present here a second SMM, called $[\text{Mn}_{12}]^{2-}$, that clearly shows quantum phase interference effects.

The $[\text{Mn}_{12}]^{2-}$ SMM was prepared from $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]$ (Mn_{12} acetate)² by a ligand substitution procedure and converted to $(\text{PPh}_4)_2[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCHCl}_2)_{16}(\text{H}_2\text{O})_4]$ by a two-electron reduction with two equivalents of PPh_4^+I^- . The crystal structure (Fig. 1) shows that the two added electrons are on Mn^{2+} ions Mn_9 and Mn_{11} giving a 2 Mn^{2+} , 6 Mn^{3+} , 4 Mn^{4+} description.²³ The compound has a $S=10$ spin ground state and negative (Ising type) magnetoanisotropy.

The simplest model describing the spin system of $[\text{Mn}_{12}]^{2-}$ has the following Hamiltonian

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

where 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 \mathbf{H} . This Hamiltonian defines hard, medium, and easy axes of magnetization in x , y , and z directions, respectively. It has an energy level spectrum with $(2S+1)=21$ values which, to a first approximation, can be labeled by the quantum numbers $m = -10, -9, \dots, 10$ taking the z axis as the quantization axis. The energy spectrum can be obtained by

using standard diagonalization techniques of the $[21 \times 21]$ matrix. At $\mathbf{H}=0$, the $m = \pm 10$ levels 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 (a field applied perpendicular to the z direction) 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 by³

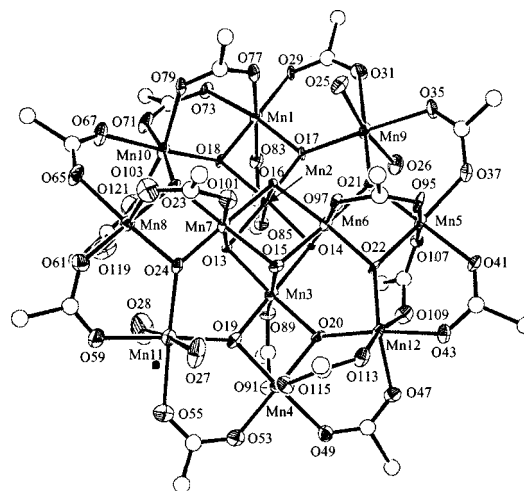


FIG. 1. Oak Ridge Thermal Ellipsoid Plot (ORTEP) representation of the complex anion $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCHCl}_2)_{16}(\text{H}_2\text{O})_4]^{2-}$ showing 50% percent probability ellipsoids. The white open circles represent C atoms. For clarity, all H and Cl atoms have been omitted.

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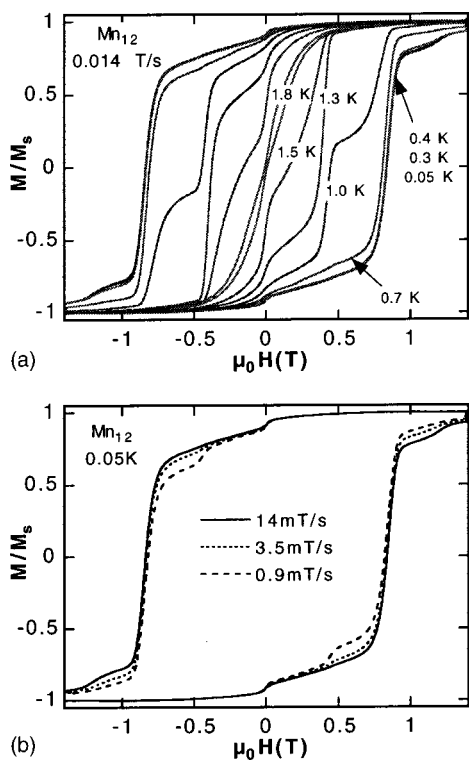


FIG. 2. Hysteresis loops of a single crystal of $[\text{Mn}_{12}]^{2-}$ molecular clusters at (a) different temperatures and a constant field sweep rate and (b) 0.05 K and different field sweep rates. Note the great difference of tunneling rate between the resonance at 0.43 and 0.85 T that establishes the parity of the wave functions involved in the tunneling process. This is quite different compared to Mn_{12} acetate showing a gradual increase of the tunneling probabilities.

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

The oscillations are explained by constructive or destructive interference of quantum spin phases (Berry phases) of two tunnel paths.³

All measurements were performed using an array of micro-superconducting quantum interference devices.²⁴ The high sensitivity of this magnetometer allows the study of single crystals of SMMs with sizes of the order of 10 to 500 μm . The field can be applied in any direction by separately driving three orthogonal coils.

Figures 2(a) and 2(b) show typical hysteresis loop measurements on a single crystal of $[\text{Mn}_{12}]^{2-}$. The effect of avoided level crossings can be seen in hysteresis loop measurements. 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 transition rate as a result of reduced thermally assisted tunneling. Below about 0.4 K, the hysteresis loops become temperature independent which suggests that the ground state tunneling is dominating. The field between two resonances allows an estimation of the anisotropy constants D , and a value of $D \approx 0.55$ K was determined.

We have tried to use the Landau-Zener method^{25,26} to measure the tunnel splitting as a function of transverse field as previously reported for Fe_8 .⁴ However, the tunnel prob-

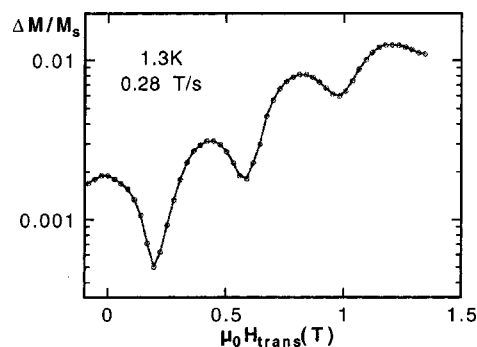


FIG. 3. Fraction of molecules which reversed their magnetization after the field was swept over the zero-field resonance. The contribution of the fast relaxing species is subtracted. The observed oscillations are direct evidence for quantum phase interference.

ability in the pure quantum regime (below 0.4 K) was too small for our measuring technique.²⁷ We therefore studied the tunnel probability in the thermally activated regime.^{28,29}

In order to measure the tunnel probability, a crystal of $[\text{Mn}_{12}]^{2-}$ SMM was first placed in a high negative field, yielding a saturated initial magnetization. Then, the applied field was swept at a constant rate over one of the resonance transitions and the fraction of molecules which reversed their spin was measured. This experiment was then repeated but in the presence of a constant transverse field. A typical result is presented in Fig. 3 showing oscillations of the tunnel probability as a function of the magnetic field applied along the hard anisotropy axis. These oscillations are due to topological quantum interference of two tunnel paths of opposite windings.³ This observation is similar to the result on the Fe_8 molecular cluster.⁴ It is therefore the second direct evidence for the topological part of the quantum spin phase (Berry phase) in a magnetic system. The period of oscillation allows an estimation of the anisotropy constant E [see Eq. (2)] and a value of $E \approx 0.06$ K was obtained.

In conclusion, magnetization measurements of a molecular cluster $[\text{Mn}_{12}]^{2-}$ with a spin ground state of $S=10$ 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. $[\text{Mn}_{12}]^{2-}$ is therefore the second molecular clusters presenting quantum phase interference.

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