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.

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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 to observe these phenomena since they have a well defined structure with well characterized spin ground state and magnetic anisotropy. The first molecule shown to be a SMM was Mn$_{12}$acetate $^1$. It exhibits slow magnetization relaxation of its spin ground state which is split by axial zero-field splitting. It was the first system to show thermally assisted tunneling $^1$. This effect was recently seen in Fe$^2$. Tunneling was also found in other SMMs (see, for instance, $^3$ $^4$ $^5$ $^6$). Quantum phase interference $^7$ is among the most interesting quantum phenomena that can be studied at the mesoscopic level in SMMs. This effect was recently observed in Fe$^8$ and Mn$_{12}$$^{2-}$ SMMs $^7$ $^8$. It has led to new theoretical studies on quantum phase interference in spin systems $^8$ $^9$ $^10$ $^11$ $^12$. It was then shown that tunneling can even be absent without Kramers degeneracy $^7$ $^10$. Quantum phase interference can lead to destructive interference and thus suppression of tunneling $^10$. This effect was recently seen in Fe$^8$ and Mn$_{12}$ SMMs $^7$ $^9$. $^{10}$ $^11$ $^12$.

There are several reasons why quantum phase interference and spin-parity effects are difficult to observe. The main reason reflects 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 superexchange 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 $^7$.

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 $^7$. The compounds are [Mn$_{12}$O$_{12}$(O$_2$CC$_6$F$_5$)$_{16}$(H$_2$O)$_4$], (NMe$_4$)[Mn$_{12}$O$_{12}$(O$_2$CC$_6$F$_5$)$_{16}$(H$_2$O)$_4$], and (NMe$_4$)$_2$[Mn$_{12}$O$_{12}$(O$_2$CC$_6$F$_5$)$_{16}$(H$_2$O)$_4$] (called Mn$_{12}$, [Mn$_{12}$]$^2-$, and [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, [Mn_{12}]^{-} and [Mn_{12}]^{2-}, respectively. The three complexes crystallize in the triclinic P1bar, monoclinic P2/c and monoclinic C2/c space groups, respectively. The molecular structures are all very similar, each consisting of a central [Mn^IVO_4] cubane core that is surrounded by a non-planar ring of eight Mn^{III} ions. Bond valence sum calculations establish that the added electrons in [Mn_{12}]^{-} and [Mn_{12}]^{2-} are localized on former Mn^{III} ions giving trapped-valence Mn^{IV}Mn^{III}Mn^{II} and Mn^{IV}Mn^{III}Mn^{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 [Mn_{12}]^{-}, and $S = 10$, $D = 0.42$ K, $g = 2.05$, for [Mn_{12}]^{2-}, where $D$ is the axial zero-field splitting parameter. 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 [Mn_{12}]^{-}, and 25 K for [Mn_{12}]^{2-}.

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

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

$S_x$, $S_y$, 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 $x$, $y$, 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 $m = -S, -(S - 1), \ldots, S$ taking the $z$-axis as the quantization axis. The energy spectrum can be obtained by using standard diagonalisation 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 $\mu_0H_z \approx nD/g\mu_B$, with $n = 0, 1, 2, 3, \ldots$.

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 $\Delta$, can be tuned by a transverse field (Fig. 1) via the $S_xH_x$ and $S_yH_y$ Zeeman terms. In the case of the transverse term $E(S_x^2 - S_y^2)$, it was shown that $\Delta$ oscillates with a period given by

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

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

All measurements were performed using an array of micro-SQUIDs [39]. The high sensitivity of this magnetometer allows the study of single crystals of SMMs with sizes of the order of 10 to 500 $\mu$m. The field can be applied in any direction by separately driving three orthogonal coils. The field was aligned using the transverse field method [40].

Fig. 2 shows typical hysteresis loop measurements on
a single crystal of the three Mn$_{12}$ samples. 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 $T_c = 0.65$ K, 0.5 K, 0.35 K, respectively for Mn$_{12}$, [Mn$_{12}$]$^-$, [Mn$_{12}$]$^{2-}$, 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 values of $D \approx 0.64$ K, 0.44 K, 0.42 K were determined (supposing $g = 2$), respectively for Mn$_{12}$, [Mn$_{12}$]$^-$, [Mn$_{12}$]$^{2-}$, being in good agreement with other magnetization studies.

We have tried to use the Landau–Zener method \cite{41, 42} to measure the tunnel splitting as a function of transverse field as previously reported for Fe$_8$ \cite{11}. However, the tunnel probability in the pure quantum regime (below $T_c$) was too small for our measuring technique \cite{43} for Mn$_{12}$ and [Mn$_{12}$]$^-$. We therefore studied the tunnel probability in the thermally activated regime \cite{11}.

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 $\varphi$ (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 $\varphi = 0^\circ$ whereas no oscillations are observed for $\varphi = 90^\circ$. These oscillations are due to topological quantum interference of two tunnel paths of opposite windings \cite{10}. The measurements of [Mn$_{12}$]$^{2-}$ are similar to the result on the Fe$_8$ molecular cluster \cite{11, 14}; 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 \cite{34}. The period of oscillation allows an estimation of the anisotropy constant $E$ (see Eq. 2) and values of $E \approx 0$, 0.047 K, and 0.086 K were obtained for Mn$_{12}$, [Mn$_{12}$]$^-$, [Mn$_{12}$]$^{2-}$, respectively.
and (b) at 0.1 K and two azimuth angles.

FIG. 5: 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 $\varphi$.

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.

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[1] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Fölting, D. Gatteschi, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. 115, 1804 (1993).
[2] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature 365, 141 (1993).
[3] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. 76, 3830 (1996).
[4] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) 383, 145 (1996).
[5] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. 78, 4645 (1997).
[6] S. M. J. Aubin, N. R. Dilley, M. B. Wemple, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. 120, 839 (1998).
[7] A. Caneschi, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, A. Cornia, M. A. Novak, C. Paulsen, and W. Wernsdorfer, J. Magn. Magn. Mat. 200, 182 (1999).
[8] D. J. Price, F. Lionti, R. Ballou, P.T. Wood, and A. K. Powell, Phil. Trans. R. Soc. Lond. A 357, 3099 (1999).
[9] J. Yoo, E. K. Brechin, A. Yamaguchi, M. Nakano, J. C. Huffman, A.L. Maniero, L.-C. Bruneel, K. Awaga, H. Ishimoto, G. Christou, and D. N. Hendrickson, Inorg. Chem. 39, 3615 (2000).
[10] A. Garg, EuroPhys. Lett. 22, 205 (1993).
[11] W. Wernsdorfer and R. Sessoli, Science 284, 133 (1999).
[12] W. Wernsdorfer, M. Soler, G. Christou, and D.N. Hendrickson, J. Appl. Phys. 91, 1 (2002).
[13] A. Garg, J. Math. Phys. 39, 5166 (1998).
[14] A. Garg, Phys. Rev. Lett. 83, 4365 (1999).
[15] A. Garg, Phys. Rev. B 60, 6705 (1999).
[16] E. Kececioglu and A. Garg, Phys. Rev. B 63, 064422 (2001).
[17] A. Garg, EuroPhys. Lett. 50, 382 (2000).
[18] S.E. Barnes, cond-mat/9907257 (2000).
[19] J. Villain and A. Fort, Euro. Phys. J. B 17, 69 (2000).
[20] J.-Q. Liang, H.J.W. Mueller-Kirsten, D.K. Park, and F.-C. Pu, Phys. Rev. B 61, 8856 (2000).
[21] Sahung-Kyoo Yoo and Soo-Young Lee, Phys. Rev. B 62, 3014 (2000).
[22] Sahung-Kyoo Yoo and Soo-Young Lee, Phys. Rev. B 62, 5713 (2000).
[23] M. N. Leuenberger and D. Loss, Phys. Rev. B 61, 12200 (2000).
[24] M. N. Leuenberger and D. Loss, Phys. Rev. B 63, 054414 (2001).
[25] Rong Lü, Hui Hu, Jia-Lin Zhu, Xiao-Bing Wang, Lee Chang, and Bing-Lin Gu, Phys. Rev. B 61, 14581 (2000).
[26] Rong Lü, Su-Peng Kou, Jia-Lin Zhu, Lee Chang, and Bing-Lin Gu, Phys. Rev. B 62, 3346 (2000).
[27] Rong Lü, Jia-Lin Zhu, Yi Zhou, and Bing-Lin Gu, Phys. Rev. B 62, 11661 (2000).
[28] Y.-B. Zhang, J.-Q. Liang, H. J. W. Müller-Kirsten, S.-P. Kou, X.-B. Wang, and F.-C. Pu, Phys. Rev. B 60, 12886 (2000).
[29] Yan-Hong Jin, Yi-Hang Nie, J.-Q. Liang, Z.-D. Chen, W.-F. Xie, and F.-C. Pu, Phys. Rev. B 62, 3316 (2000).
[30] E. M. Chudnovsky and X. Martines Hidalgo, EuroPhys. Lett. 50, 395 (2000).
[31] W. Wernsdorfer, S. Bhaduri, C. Boskovic, G. Christou, and D.N. Hendrickson, Phys. Rev. B 65, 180403 (2002).
[32] M. Enz and R. Schilling, J. Phys. C 19, L711 (1986).
[33] J. L. Van Hemmen and S. Suito, EuroPhys. Lett. 1, 481 (1986).
[34] The Kramers theorem asserts that no matter how unsymmetric the crystal field, an ion possessing an odd number of electrons must have a ground state that is at least doubly degenerate, even in the presence of crystal fields and spin-orbit interactions [H. A. Kramers, Proc. Acad. Sci. Amsterdam 33, 959 (1930)].
[35] D. Loss, D. P. DiVincenzo, and G. Grinstein, Phys. Rev. Lett. 69, 3232 (1992).
[36] J. von Delft and C. L. Henley, Phys. Rev. Lett. 69, 3236 (1992).
[37] W. Wernsdorfer, R. Sessoli, and D. Gatteschi, EuroPhys. Lett. 47, 254 (1999).
[38] N. E. Chakov, M. Soler, W. Wernsdorfer, K. A. Abboud, and G. Christou, in preparation (2005).
[39] W. Wernsdorfer, Adv. Chem. Phys. 118, 99 (2001).
[40] W. Wernsdorfer, N. E. Chakov, and G. Christou, Phys. Rev. B 70, 132413 (2004).
[41] L. Landau, Phys. Z. Sowjetunion 2, 46 (1932).
[42] C. Zener, Proc. R. Soc. London, Ser. A 137, 696 (1932).
[43] As observed for Mn_{12} acetate [37], the crystals of Mn_{12}, [Mn_{12}]^{-}, [Mn_{12}]^{2-} contain a small fraction of faster-relaxing species, which are probably molecules having a defect. The signals of these species were very large compared to the ground state relaxation rate of the major species.
[44] W. Wernsdorfer, A. Caneschi, R. Sessoli, D. Gatteschi, A. Cornia, V. Villar, and C. Paulsen, EuroPhys. Lett. 50, 552 (2000).