PHYSICAL REVIEW B, VOLUME 65, 180403(R)

Spin-parity dependent tunneling of magnetization in single-molecule magnets

W. Wernsdorfer,[1] S. Bhaduri,[2] C. Boskovic,[2] G. Christou,[2] and D. N. Hendrickson[3]
[1]*Laboratoire Louis Néel, associé à l'UJF, CNRS, BP 166, 38042 Grenoble Cedex 9, France*
[2]*Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405-4001*
[3]*Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, California 92037*
(Received 4 March 2002; published 25 April 2002)

Single-molecule magnets facilitate the study of quantum tunneling of magnetization at the mesoscopic level. The spin-parity effect is among the fundamental predictions that have yet to be clearly observed. It is predicted that quantum tunneling is suppressed at zero transverse field if the total spin of the magnetic system is half-integer (Kramers degeneracy) but is allowed in integer spin systems. The Landau-Zener method is used to measure the tunnel splitting as a function of transverse field. Spin-parity dependent tunneling is established by comparing the transverse field dependence of the tunnel splitting of integer and half-integer spin systems.

DOI: 10.1103/PhysRevB.65.180403 PACS number(s): 75.45.+j, 75.60.Ej

Single-molecule magnets (SMM) are considered the best systems for studying quantum tunneling of magnetization at the mesoscopic level. The first molecule shown to be a SMM was Mn_{12} acetate.[1] It exhibits slow magnetization relaxation of its $S=10$ ground state that 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 SMM's were the first to exhibit ground-state tunneling.[4,5] Tunneling was also found in other SMM's (see, for instance, Refs. 6–8). A detailed study of the influence of environmental degrees of freedom on the tunneling process is in progress on Fe_8 and Mn_{12} acetate (concerning phonons[9,10], nuclear spins, and dipolar couplings,[11–13]), which is motivated by theoretical considerations.[14–16] The spin-parity effect is among the fundamental predictions that have yet to be established at the mesoscopic level. It 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. Van Hemmen and Süto[17] were the first to suggest the absence of tunneling as a consequence of the Kramers degeneracy.[18] It was then shown that tunneling can even be absent without the Kramers degeneracy;[19–21] quantum phase interference can lead to destructive interference and thus suppression of tunneling.[21] This effect was recently seen in Fe_8 and Mn_{12} SMM's.[22,23]

There are several reasons why the first attempts[5,24] to observe the spin-parity effect were unsuccessful. The main reason reflects the influence of environmental degrees of freedom that can induce or suppress tunneling. The 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.[12]

In this Communication, we show that these problems can be overcome by studying the tunnel splitting as a function of transverse field. From an investigation of more than 20 SMM's, we selected three systems that are sufficiently well known to allow a straightforward comparison. The complete study will be reported elsewhere.

The first SMM is $[Mn_4O_3(OSiMe_3)(OAc)_3(dbm)_3]$, called Mn_4 $(S=9/2)$, with a half-integer ground state $S=9/2$. The second is $[Mn_4(OAc)_2(Hpdm)_6][ClO_4]_2$, called Mn_4 $(S=8)$, with an integer ground state $S=8$. The third is the well known Fe_8 SMM with a $S=10$ ground state.[4] The preparation, x-ray structure, and detailed physical characterization of both Mn_4 molecules have been reported.[8,25] Mn_4 $(S=9/2)$ crystallizes in a hexagonal space group with crystallographic C_3 symmetry. The complex has a trigonal-pyramidal (highly distorted cubanelike) geometry and is mixed valent, $Mn_3^{III}Mn^{IV}$. The C_3 axis passes through the Mn^{IV} ion and the triply bridging siloxide group. The dc and ac magnetic-susceptibility measurements indicate a well isolated $S=9/2$ ground state.[25] Mn_4 $(S=8)$ crystallizes in a triclinic lattice. The cation lies on an inversion center and consists of a planar Mn_4 rhombus that is also mixed valent, $Mn_2^{II}Mn_2^{III}$. The dc and ac magnetic-susceptibility measurements indicate a $S=8$ ground state.[8]

All measurements were performed using an array of micro-superconducting quantum interference devices (micro-SQUID's).[11] The high sensitivity allows us to study single crystals of SMM's of the order of 10–500 μm. The field can be applied in any direction by separately driving three orthogonal coils.

We first review briefly the giant spin model that is the simplest model describing the spin system of SMM's. The spin Hamiltonian is

$$\mathcal{H}=-DS_z^2+\mathcal{H}_{\text{trans}}+g\mu_B\mu_0\vec{S}\cdot\vec{H}, \tag{1}$$

Where S_x, S_y, and S_z are the components of the spin operator; D is the anisotropy constant defining an Ising-type of anisotropy; $\mathcal{H}_{\text{trans}}$, containing S_x or S_y spin operators, gives the transverse anisotropy that is small compared to DS_z^2 in SMM's; and the last term describes the Zeeman energy associated with an applied field $\vec{H}$, where $g\approx 2$ and μ_B is the Bohr magneton. This Hamiltonian has an energy-level spectrum with $2S+1$ values that, 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 diagonalization techniques. At $\vec{H}=0$, the levels $m=\pm S$ have the lowest energy.

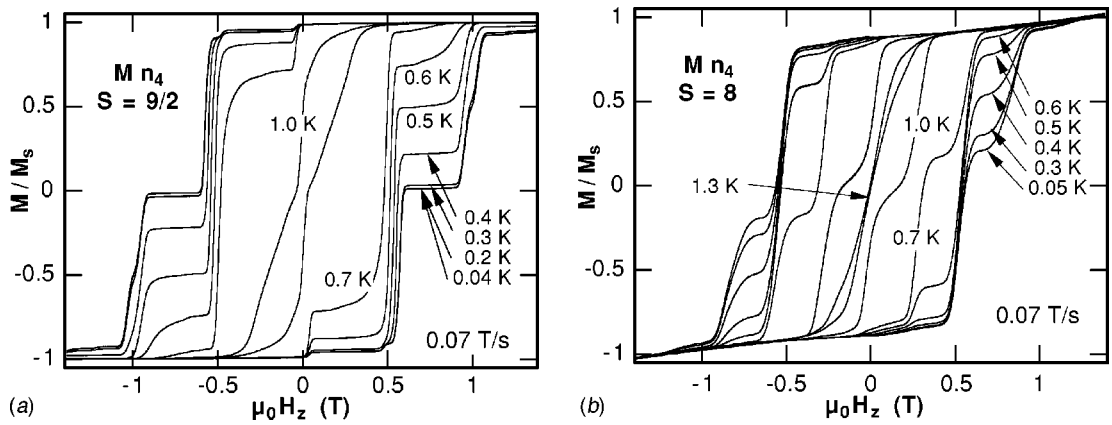

FIG. 1. Hysteresis loops of a single crystal of (a) Mn_4 ($S=9/2$) and (b) Mn_4 ($S=8$) molecular clusters at different temperatures and a constant field sweep rate $dH_z/dt=0.07$ T/s.

When a field H_z is applied, the levels with $m>0$ decrease in energy, while those with $m<0$ increase. Therefore, energy levels of positive and negative quantum numbers cross at certain values of H_z given by $\mu_0 H_z \approx nD/g\mu_B$, where $n=0,1,2,3,\ldots$.

When the spin Hamiltonian contains transverse terms ($\mathcal{H}_{trans}$), 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 S_z direction) via the S_xH_x and S_yH_y Zeeman terms.

The effect of these avoided level crossings can be seen in hysteresis loop measurements. Figures 1(a) and 1(b) show typical hysteresis loops for single crystals of Mn_4 ($S=9/2$) and Mn_4 ($S=8$). 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 due to reduced thermally assisted tunneling. A similar behavior was observed in other SMM's.[2–13] The hysteresis loops become temperature independent below 0.4 K indicating ground-state tunneling. The field between two resonances allows us to estimate the anisotropy constant D. We obtain 0.68 K and 0.43 K for Mn_4 ($S=9/2$) and Mn_4 ($S=8$), respectively.

In order to establish the spin-parity effect, the tunnel splitting was measured as a function of transverse field. The field dependence of the tunnel splitting is expected to be very sensitive to the spin-parity and the parity of the avoided level crossing. This approach is based on the Landau-Zener (LZ) model that describes the nonadiabatic transition between the two states in a two-level system.[26,27] The solution of the time-dependent Schrödinger equation of a two-level system can be applied to many physical systems and it has become an important tool for studying tunneling transitions. The LZ model has also been applied to spin tunneling in nanoparticles and clusters.[28–32]

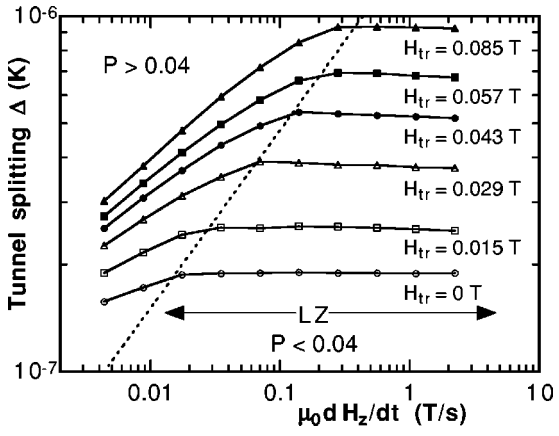

FIG. 2. Field sweep rate dependence of the tunnel splitting $\Delta_{-9/2,9/2}$ measured by a Landau-Zener method for Mn_4 ($S=9/2$) samples at different transverse fields. The Landau-Zener method works in the region of high sweep rates (typically for $P<0.04$) where $\Delta_{-9/2,9/2}$ is sweep rate independent.

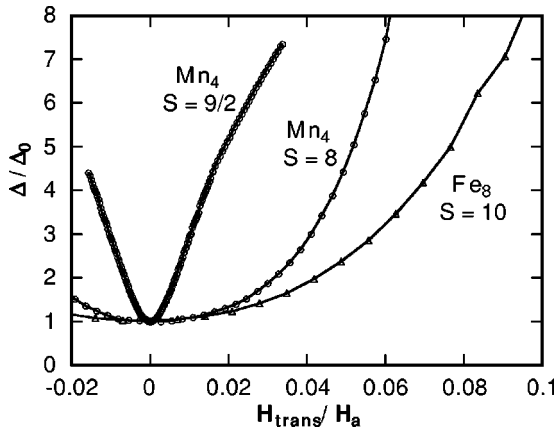

FIG. 3. Tunnel splitting for three SMM's as a function of transverse field. The tunnel splitting is normalized by $\Delta_0=1.9$, 0.94, and 0.28×10^{-7} K, and the transverse field is normalized by the anisotropy field $H_a=2DS/g\mu_B=4.6$, 5.1, and 4.0 T for Mn_4 ($S=9/2$), Mn_4 ($S=8$), and Fe_8, respectively. The data for Fe_8 were taken from Ref. 22 with the transverse field applied along the medium hard axis.

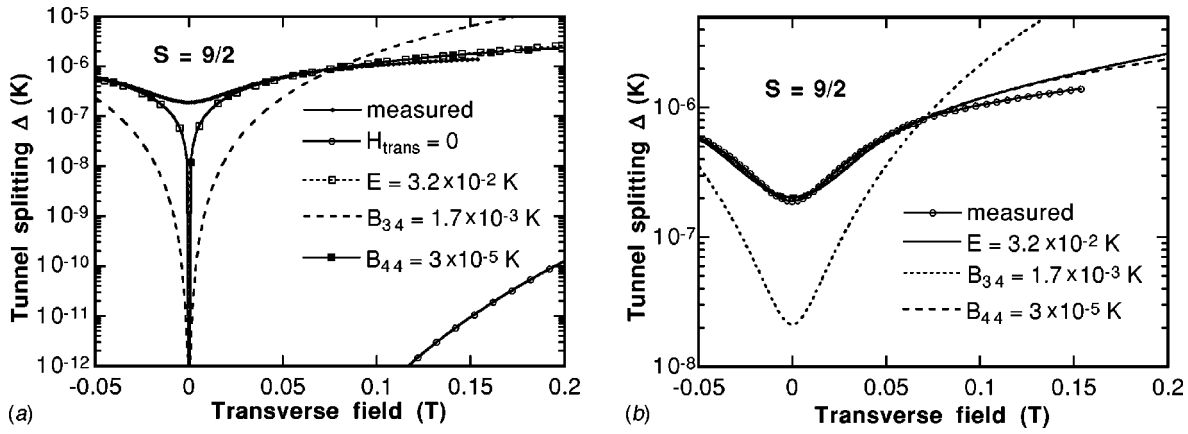

FIG. 4. (a) Simulation of the measured tunnel splittings for Mn_4 ($S=9/2$). For simplicity, the calculated Δ has been averaged over all possible orientations of the transverse field. (b) Same as in (a) but taking into account a Gaussian distribution of the transverse field components with a half-width $\sigma=0.035$ T.

When sweeping the longitudinal field H_z at a constant rate over an avoided energy-level crossing, the tunneling probability P is given by

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

Here, m and m' are the quantum numbers of the avoided level crossing, dH_z/dt is the constant field sweep rate, and $\hbar$ is Planck's constant.

In order to apply quantitatively the LZ formula [Eq. (2)], we first checked the predicted sweep field dependence of the tunneling rate. The SMM crystal was placed in a high negative field to saturate the magnetization, the applied field was swept at a constant rate over one of the resonance transitions, and the fraction of molecules that reversed their spin was measured. The tunnel splitting Δ was calculated using Eq. (2) and is plotted in Fig. 2 as a function of the field sweep rate. The LZ method is applicable in the region of high sweep rates where $\Delta_{-9/2,9/2}$ is independent of sweep rate. The deviations at lower sweep rates are mainly due to the *hole-digging mechanism*[11] as observed for Fe_8.[10] Such behavior has recently been simulated.[33,34]

Figure 3 presents the tunnel splittings obtained by the LZ method as a function of transverse field. Mn_4 ($S=9/2$) and Mn_4 ($S=8$) did not show a clear dependence on the direction of the transverse field. Note that for all three SMM's the tunnel splitting is finite at applied zero transverse field. However, depending on the spin-parity the sensitivity to an applied transverse field is completely different. The tunnel splitting increases gradually for an integer spin, whereas it increases rapidly for a half-integer spin. Note also that the tunnel probability depends on the second power of Δ [Eq. 2]. Therefore, these data show that the tunneling rate of a half-integer spin is strongly transverse field dependent, unlike the case for an integer spin SMM.

Figures 4(a) and 4(b) present the simulation of the measured tunnel splittings for Mn_4 ($S=9/2$). First, one should note that there must be transverse terms in the spin Hamiltonian because for $\mathcal{H}_{\rm trans}=0$, the measured tunnel splitting should be orders of magnitude smaller than observed. Second, we tried to simulate the data with a transverse term $(B_{34}/2[S_z(S_+^3+S_-^3)+(S_+^3+S_-^3)S_z])$ with respect to the C_3 symmetry of the SMM, but this term cannot account for the measured tunnel splitting. However, we found that either the second-order term $[E(S_+^2+S_-^2)]$ or a fourth-order term $[B_{44}(S_+^4+S_-^4)]$ can describe equally well the experimental data.[35] These results suggest that there is a small effect that breaks the C_3 symmetry. This could be a small strain inside the SMM crystal induced by defects, which could result from a loss or disorder of solvent molecules, or from dislocations.[36] This interpretation is in agreement with the fact that we did not find a clear dependence of Δ on the direction of the transverse field. Indeed, one would expect a distribution of transverse anisotropy directions. Recent inelastic-neutron-scattering measurements confirm the presence of second- and fourth-order terms.[25]

In an ideal case, one would expect $\Delta=0$ for $\vec{H}=0$. This is not found in a real SMM because of the influence of the environmental degrees of freedom that can induce tunneling. In our case, mainly hyperfine and dipolar couplings induce tunneling via transverse field components. Figure 4(b) presents a simulation of the measured tunnel splitting when taking into account a Gaussian distribution of transverse field components with a width $\sigma=0.035$ T. This value is in good agreement with other SMM's.

The simulation of measured tunnel splittings for Mn_4 ($S=8$) is much easier because an integer spin is not very sensitive to transverse field components resulting from hyperfine and dipolar couplings. We found that a second-order term with $E=0.057$ K can describe the data well.

In conclusion, we have shown that the predicted spin-parity effect[17–20] can indeed be observed by measuring the tunnel splitting as a function of transverse field. An integer

spin system is rather insensitive to small transverse fields whereas a half-integer spin systems is much more sensitive. However, a half-integer spin system will also undergo tunneling at zero external field as a result of environmentaldegrees of freedom, such as hyperfine and dipolar couplings or small intermolecular superexchange interaction.

I. Tupitsyn and M. Elhajal are acknowledged for fruitful discussions; and C. Thirion, D. Mailly, and A. Benoit for support to the micro-SQUID technique. This work was supported by the European Union TMR network MOLNA-NOMAG, HPRN-CT-1999-0012, and the USA National Science Foundation (Contract No. DMR-0103290).

[1] R. Sessoli, D. Gatteschi, A. Caneschi, and M.A. Novak, Nature (London) **365**, 141 (1993).
[2] J.R. Friedman, M.P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).
[3] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).
[4] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).
[5] S.M.J. Aubin, N.R. Dilley, M.W. Wemple, M.B. Maple, G. Christou, and D.N. Hendrickson, J. Am. Chem. Soc. **120**, 839 (1998).
[6] A. Caneschi, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, A. Cornia, M.A. Novak, C. Paulsen, and W. Wernsdorfer, J. Magn. Magn. Mater. **200**, 182 (1999).
[7] D.J. Price, F. Lionti, R. Ballou, P.T. Wood, and A.K. Powell, Philos. Trans. R. Soc. London, Ser. A **357**, 3099 (1999).
[8] J. Yoo, E.K. Brechin, A. Yamaguchi, M. Nakano, J.C. Huffman, A.L. Maniero, L.-C. Brunel, K. Awaga, H. Ishimoto, G. Christou, and D.N. Hendrickson, Inorg. Chem. **39**, 3615 (2000).
[9] L. Bokacheva, A.D. Kent, and M.A. Walters, Phys. Rev. Lett. **85**, 4803 (2000).
[10] W. Wernsdorfer, A. Caneschi, R. Sessoli, D. Gatteschi, A. Cornia, V. Villar, and C. Paulsen, Europhys. Lett. **50**, 552 (2000).
[11] W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, and C. Paulsen, Phys. Rev. Lett. **82**, 3903 (1999).
[12] W. Wernsdorfer, R. Sessoli, and D. Gatteschi, Europhys. Lett. **47**, 254 (1999).
[13] W. Wernsdorfer, A. Caneschi, R. Sessoli, D. Gatteschi, A. Cornia, V. Villar, and C. Paulsen, Phys. Rev. Lett. **84**, 2965 (2000).
[14] A. Fort, A. Rettori, J. Villain, D. Gatteschi, and R. Sessoli, Phys. Rev. Lett. **80**, 612 (1998).
[15] E.M. Chudnovsky and D.A. Garanin, Phys. Rev. Lett. **79**, 4469 (1997).
[16] N.V. Prokof'ev and P.C.E. Stamp, Phys. Rev. Lett. **80**, 5794 (1998).
[17] J.L. Van Hemmen and S. Süto, Europhys. Lett. **1**, 481 (1986).
[18] 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. R. Acad. Sci. Amsterdam **33**, 959 (1930)]. The Kramers theorem can be found in standard textbooks on quantum mechanics [L.D. Landau and E.M. Lifschitz, *Quantum Mechanics* (Pergamon, London, 1959].
[19] D. Loss, D.P. DiVincenzo, and G. Grinstein, Phys. Rev. Lett. **69**, 3232 (1992).
[20] J. von Delft and C.L. Henley, Phys. Rev. Lett. **69**, 3236 (1992).
[21] A. Garg, Europhys. Lett. **22**, 205 (1993).
[22] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).
[23] W. Wernsdorfer, M. Soler, G. Christou, and D.N. Hendrickson, J. Appl. Phys. **1**, 1 (2002).
[24] A.M. Gomes, M.A. Novak, W. Wernsdorfer, R. Sessoli, L. Sorace, and D. Gatteschi, J. Appl. Phys. **87**, 6004 (2000).
[25] S. Bhaduri, M. Pink, K. Folting, W. Wernsdorfer, A. Sieber, H. U. Güdel, D. N. Hendrickson, and G. Christou (unpublished).
[26] L. Landau, Phys. Z. Sowjetunion **2**, 46 (1932).
[27] C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932).
[28] S. Miyashita, J. Phys. Soc. Jpn. **64**, 3207 (1995).
[29] S. Miyashita, J. Phys. Soc. Jpn. **65**, 2734 (1996).
[30] G. Rose and P.C.E. Stamp, Low Temp. Phys. **113**, 1153 (1998).
[31] M. Thorwart, M. Grifoni, and P. Hänggi, Phys. Rev. Lett. **85**, 860 (2000).
[32] M.N. Leuenberger and D. Loss, Phys. Rev. B **61**, 12 200 (2000).
[33] Jie Liu, Biao Wu, Li-Bin Fu, Roberto B. Diener, and Qian Niu, cond-mat/0105497 (unpublished).
[34] A more detailed study shows that the tunnel splittings obtained by the LZ method are slightly influenced by environmental effects like hyperfine and dipolar couplings (Refs. 10 and 33). Therefore, one might call it an effective tunnel splitting.
[35] The fit could be improved by using a combination of transverse terms but this does not lead to a better insight concerning the spin-parity effect.
[36] E.M. Chudnovsky and D.A. Garanin, Phys. Rev. Lett. **87**, 187203 (2001).