Asymmetric Berry-Phase Interference Patterns in a Single-Molecule Magnet
H. M. Quddusi, J. Liu, S. Singh, K. J. Heroux, E. del Barco, S. Hill, and D. N. Hendrickson
Phys. Rev. Lett. 106, 227201 — Published 31 May 2011
DOI: 10.1103/PhysRevLett.106.227201
Asymmetric Berry-Phase Interference Patterns in a Single-Molecule Magnet

H. M. Qudusu1, J. Liu2, S. Singh1, K. J. Heroux4, E. del Barco1, S. Hill3, and D. N. Hendrickson4

1Department of Physics, University of Central Florida, Orlando, FL 32816, USA
2Department of Physics, University of Florida, Gainesville, FL 32611, USA
3National High Magnetic Field Laboratory and Department of Physics, Florida State University, Tallahassee, FL 32310, USA and
4Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 92093, USA

A Mn₄ single-molecule magnet displays asymmetric Berry-phase interference patterns in the transverse-field (H₉) dependence of the magnetization tunneling probability when a longitudinal field (H₇) is present, contrary to symmetric patterns observed for H₇ = 0. Reversal of H₇ results in a reflection of the transverse-field asymmetry about H₉ = 0, as expected on the basis of the time-reversal invariance of the spin-orbit Hamiltonian which is responsible for the tunneling oscillations. A fascinating motion of Berry-phase minima within the transverse field magnitude-direction phase space results from a competition between non-collinear magneto-anisotropy tensors at the two distinct Mn sites.

PACS numbers: 75.45.+j, 75.50.Xx

Almost two decades of research have established single-molecule magnets (SMMs) as prototype systems for understanding fundamental quantum phenomena associated with nanoscale magnetism [1, 2], as well as demonstrating their potential for future applications [3]. The most important characteristics of SMMs can be modeled reliably using a giant-spin approximation (GSA) whereby the molecule is treated as a rigid magnetic unit with total spin, S, weakly interacting with its environment. Indeed, this model accounts for the essential features of the quantum tunneling of magnetization (QTM) observed in these molecules, as well as its quenching due to Berry phase interference (BPI) resulting from different tunneling trajectories [4–6]. However, the GSA ignores the internal couplings within a SMM, thereby completely failing to account for QTM transitions that involve fluctuations of the total spin of the molecule [7–9], or otherwise obscuring intrinsic relationships that exist between QTM selection rules and the underlying molecular structure [10]. In a recent interesting example, it was demonstrated that a tilting of the zero-field splitting (zfs) tensors in a triangular Mn₃⁢II SMM (lowering the symmetry of the spin Hamiltonian from C₆ to C₃) results in new QTM selection rules and strongly affects the transverse field dependence of the remaining forbidden QTM resonances [10]. These observations likely explain the absence of QTM selection rules in most SMMs studied to date, since internal dipolar fields and/or weak sample disorder are often sufficient to cause observable relaxation at resonances otherwise forbidden by symmetry. A detailed understanding of these and related phenomena has mostly been facilitated by studies of low nuclearity SMMs [11, 12], where exact diagonalization of the multi-spin Hamiltonian enables consideration of the internal degrees of freedom of the molecule.

In this letter, we focus on the QTM relaxation associated with a centro-symmetric mixed-valent Mn₂⁺Mn₂⁻ complex which shows an asymmetric BPI pattern with respect to the polarity of the transverse component of the applied field (H₉ ⊥ magnetic easy axis). We show that this behavior results from a competition between non-collinear magneto-anisotropy tensors at the two crystallographically distinct Mn ions, which is also responsible for an unusual motion of the Berry-phase minima within the transverse field magnitude-direction phase space. We show how the asymmetry can be inverted upon reversal of the longitudinal field (H₇ || easy axis), i.e., the BPI pattern is invariant with respect to a full inversion of the
applied field, consistent with the time-reversal symmetry of the underlying zero-field Hamiltonian.

The [Mn4(Bet)4(me-dea)2(Hme-dea)2](BPh4)4 complex (henceforth Mn4-Bet) crystallizes in the triclinic P1 space group with half the molecule in the asymmetric unit; the other half is generated via inversion, resulting in the four Mn ions lying in a plane (the molecular plane), with the Mn111 Jahn-Teller (JT) axes oriented along the Mn111-N bonds, which lie 122.61 degrees out of this plane, i.e., roughly perpendicular to the molecular plane [13, 14]. There are no solvent groups in the lattice and the four BPh4 anions enhance isolation, resulting in extremely clean X-ray diffraction and EPR data [14, 15]. A sketch of the Mn4 core, where the magnetic axes are indicated, is inset to Fig. 1. Magnetic and EPR measurements performed at relatively high temperatures \((T > 2 \text{ K})\) suggest a spin \(S = 9\) ground state, and that Mn4-Bet is a SMM with a barrier of \(\sim 20 \text{ K}\) [14].

A high-sensitivity micro-Hall effect magnetometer, a He3/He4 dilution fridge and a 3D vector superconducting magnet were employed to record magnetization hysteresis curves as a function of a magnetic field applied parallel to the easy axis of the molecules [16], at temperatures down to 35 mK. The results are shown in Fig. 1, where extremely sharp QTM resonances \((k = 0, 1 & 2)\), spaced by \(\Delta H_L \approx 0.21 \text{ T}\), confirm the high quality of the crystal. Within the GSA, this spacing corresponds to an axial zfs parameter, \(D = -0.28 \text{ K} (g = 2)\). The observed blocking and crossover temperatures are \(\sim 1.2 \text{ K}\) and \(\sim 0.2 \text{ K}\), respectively. A transverse field was subsequently employed in order to study the symmetry of the QTM in resonances \(k = 0\) and \(k = 1\). Fig. 2a shows the modulation of the QTM probability, \(P_k = (M_f - M_i)/(M_{sat} - M_i)\) [17], for resonance \(k = 0\), as a function of \(H_T\) applied along the magnetic hard axis \((\phi = 0^\circ)\). This angle, which lies \(\sim 30^\circ\) away from one of the crystal faces, was deduced from the two-fold modulation of \(P_0\) as a function of the orientation, \(\phi\), of a 0.2 T transverse field within the hard plane (see inset to Fig. 2a) [18].

The \(P_0\) oscillations in Fig. 2a correspond to BPI, with minima at regularly spaced field values \((\Delta H_T = 0.3 \text{ T})\). A maximum in \(P_0\) is found at \(H_T = 0\), as expected for an integer spin value. Within the GSA, \(\Delta H_T = 2k_B(2E[E + D])^{1/2}/g\mu_B [19]\), yielding a 2nd-order rhombic zfs parameter, \(E = \pm 60 \text{ mK}\). Note that the regularly spaced \(k = 0\) BPI minima are invariant under inversion of \(H_T\), i.e., they are symmetric with respect to \(H_T = 0\).

Interestingly, this is not the case in resonance \(k = 1\), for which the behavior of the QTM probability is very different. This can be seen in Fig. 2b, which illustrates the dependence of \(P_1\) on \(H_T\), for \(\phi = 13.5^\circ\) (the angle for which the first BPI minimum at \(H_T = 0.30 \text{ T}\) is the sharpest). In fact, for resonance \(k = 1\), different BPI minima appear at different field orientations, \(\phi\), of the transverse field within the \(xy\) (hard) plane of the molecule (see Fig. 3) [18], i.e., the first minimum \((H_T = 0.3 \text{ T})\) appears at \(\phi = 13.5^\circ\), while the second \((H_T = 0.6 \text{ T})\) occurs at \(\phi = 6^\circ\), contrary to what is found for the \(k = 0\) resonance (all \(P_0\) minima are seen most clearly at \(\phi = 0^\circ\)). Such behavior has been predicted theoretically [20, 21], though never observed experimentally.

Before considering this aspect in detail, we first discuss the asymmetric nature of the BPI oscillation pattern in resonance \(k = 1\). As seen clearly in Fig. 2b, reversal of the longitudinal field, \(H_L\), results in a reflection of the \(P_1\) BPI pattern about \(H_T = 0\). In other words, the BPI minima are in fact invariant under a full magnetic field inversion, as required on the basis of the time-reversal invariance of the spin-orbit Hamiltonian responsible for this physics. As noted above, the symmetries of BPI patterns must respect the symmetry of the zero-field spin Hamiltonian. If one considers only 2nd-order zfs within the GSA, then the resulting Hamiltonian necessarily belongs to the orthorhombic point group and possesses the following symmetry elements: (1) three mutually orthogonal two-fold rotation axes \((x, y & z)\); (2) three mutually orthogonal mirror planes \((xy, xz & yz)\); and (3) an inversion center. (2) guarantees invariance with respect to reversal of \(H_T\), i.e., it enforces symmetric BPI patterns, irrespective of whether a longitudinal field is applied \((k > 0)\) or not \((k = 0)\). As we show below, one must
break the \(xy\) mirror symmetry in order to obtain asymmetric BPI patterns with respect to inversion of \(H_T\). In this case, reversal of \(H_L\) results in different patterns; the time reversal symmetry then guarantees that these two patterns are mirror images. Nevertheless, no matter how many spatial symmetries are broken, the time-reversal invariance of the spin-orbit interaction guarantees that the BPI minima should be invariant under a full reversal of the applied field, i.e., simultaneous reversal \(H_L\) and \(H_T\), as we have confirmed experimentally.

It is possible to reproduce the essential features of the experiments by introducing 4th-order terms into the GSA; the \(xy\) mirror symmetry can then be broken by rotating the coordinate frames of the 2nd and 4th-order tensors. Interestingly, this approach also reproduces the complex motion of the experimental field rotation plane \[18\], employed the following parameters: \(d_2 = d_4 = -4.99\) K and \(e_2 = e_4 = 0.82\) K, with the easy and hard anisotropy axes along \(z\) \((\alpha_2 = 0)\) and \(x\) \((\beta_2 = 0)\), respectively; \(d_1 = d_3 = -0.67\) K & \(e_1 = e_3 = 0\), with the axes rotated with respect to the central spin by identical Euler angles \(\alpha_{1,3} = 45^\circ\), \(\beta_{1,3} = 0^\circ\) (as required by inversion symmetry); \(\gamma\) being zero for all ions; finally, isotropic ferromagnetic exchange constants \(J_a = -3.84\) K, \(J_b = -1.20\) K and \(J_c = -3.36\) K are used. It should be stressed that these parameters are additionally constrained by the locations of hysteresis loop steps (Fig. 1) and extensive angle-dependent EPR measurements \[15\]. Moreover, the obtained anisotropy values for the Mn\(^{III}\) ions are very similar to related Mn\(^{III}\) complexes \[10\], while the \(d_{1,3}\) value lies within the bounds reported for other Mn\(^{III}\) systems \[23\]. The quantitative agreement with experiment is also excellent. The motion of the \(P_1\) minima can be understood as a result of the competition between different anisotropic interactions within the molecule, without a need to invoke unphysical 4th and higher order anisotropies. Importantly, the angular positions \((\phi)\) of the \(k = 0\) minima move with \(H_T\), while the \(k = 0\) minima remain stationary, as found experimentally (Fig. 3).

Finally, the multi-spin model perfectly reproduces the
clearly demonstrates how studies of simple low nuclearity systems can address fundamental symmetry considerations related to QTM in molecular nanomagnetism.

ACKNOWLEDGEMENTS

The authors acknowledge support from NSF, specifically H.M.Q, S.S and E.d.B. from DMR-0747587, J.L. and S.H from DMR-0804408, and K.J.H and D.N.H. from CHE-0714488, and from the University of Florida High-Performance Computing Center for providing computational resources and support (URL: http://hpc.ufl.edu).

[1] E. M. Chudnovsky and J. Tejada, “Macroscopic Quantum Tunneling of Magnetic Moment”, Cambridge Univ. Press (1998).
[2] D. Gatteschi, R. Sessoli, J. Villain, “Molecular Nanomagnets”, Oxford Univ. Press (2008).
[3] M. N. Leuenberger and D. Loss, Nature 410, 789 (2001).
[4] W. Wernsdorfer, R. Sessoli, Science 284, 133 (1999).
[5] E. del Barco, A. D. Kent, E. M. Rumberger, D. N. Hendrickson and G. Christou, Phys. Rev. Lett. 91, 047203 (2003).
[6] Foss-Feig, M. S., and J. R. Friedman, Europhys. Lett. 86, 27002 (2009).
[7] C. M. Ramsey et al., Nature Physics 4, 277 (2008).
[8] S. Carreta et al., Phys. Rev. Lett. 100, 157203 (2008).
[9] S. Bahr et al., Phys. Rev. B 78, 132401 (2008).
[10] J. J. Henderson et al., Phys. Rev. Lett. 103, 017202 (2009).
[11] S. Hill et al., Dalton Trans. 39, 4693-4707 (2010).
[12] A. Wilson et al., Phys. Rev. B 74, R140403 (2006).
[13] The CIF file (CCDC 790437) has been deposited with the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data-request/cif.
[14] K. J. Heroux et al., in preparation.
[15] See EPAPS Document No. [xxxx] for the high-frequency EPR spectra recorded on this complex, as well as fits to the multi-spin Hamiltonian given in the text.
[16] The magnetic axes were determined experimentally from the angular field behavior of the QTM resonances.
[17] $M_i$ and $M_f$ are the magnetizations before and after the resonance, respectively. $M_{sat}$ is the saturation value.
[18] We note that there was a small ($\sim 3^\circ$) misalignment of the field rotation plane during the measurements. This slightly influences, but is not the primary cause of, the BPI minima motion. Simulations demonstrate that similar results are obtained when $H_T$ is rotated exactly within the $xy$ plane, for which the $k = 1$ first and second BPI minima are found at $\phi = 7.5^\circ$ and $\phi = 3^\circ$, respectively.
[19] A. Garg, Europhys. Lett. 22, 205 (1993).
[20] E. del Barco et al., J. Low Temp. Phys. 140, 119 (2005).
[21] K. Hijii and S. Miyashita, Phys. Rev. B 78, 214434 (2008).
[22] J. Liu et al., unpublished.
[23] J. Krzystek, A. Ozarowski, and J. Telser, Coord. Chem. Rev. 250, 2308 (2006).
[24] E. del Barco et al., Phys. Rev. B 82, 104426 (2010).