Spin-Spin Cross Relaxation in Single-Molecule Magnets

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The one-body tunnel picture of single-molecule magnets (SMMs) is not always sufficient to explain the measured tunnel transitions. An improvement to the picture is proposed by including also two-body tunnel transitions such as spin-spin cross relaxation (SSCR) which are mediated by dipolar and weak superexchange interactions between molecules. A Mn_4 SMM is used as a model system. At certain external fields, SSCRs lead to additional quantum resonances which show up in hysteresis loop measurements as well-defined steps. A simple model is used to explain quantitatively all observed transitions.

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Single-molecule magnets (SMMs) [1] are one of the best systems for studying quantum tunneling of large moments. Each molecule functions as a nanoscale, single-domain magnetic particle that, below its blocking temperature, exhibits the classical macroscale property of a magnet, namely, magnetization hysteresis. Such a molecule straddles the classical/quantum interface in also displaying quantum tunneling of magnetization [2–7] and quantum phase interference [8,9]. Most theoretical work until now treats crystals of SMMs as consisting of giant spins interacting with environmental degrees of freedom such as magnetic fields, phonons, and nuclear spins (see references in [10,11]). Interactions between SMMs were mainly restricted to dipolar couplings which can lead to square root relaxation laws [12] and magnetic ordering [10,11].

Since SMMs occur as assemblies in crystals, there is the possibility of a small electronic interaction of adjacent molecules. This leads to very small superexchange interactions (or exchange interactions, for short) that depend strongly on the distance and the nonmagnetic atoms in the exchange pathway. Until now, such an intermolecular exchange interaction has been assumed to be negligibly small. However, our recent studies on about 50 SMMs suggest that in most SMMs exchange interactions lead to a significant influence on the tunnel process. Recently, this intermolecular exchange interaction was used to couple antiferromagnetically two SMMs, each acting as a bias on its neighbor, resulting in quantum behavior different from that of individual SMMs [13].

In this Letter, we show that dipolar and/or exchange interactions can lead to collective quantum processes. The one-body tunnel picture of SMMs is therefore not always sufficient to explain the measured tunnel transitions. We propose to improve the picture by including also two-body tunnel transitions such as spin-spin cross relaxation (SSCR) [14,15]. A simple model allows us to explain quantitatively all observed transitions. Including three-body transitions or dealing with the many-body problem is beyond the scope of this paper.

The SMM has the formula $[Mn_4O_3(OSiMe_3)(OAc)_3(dbm)_3]$, called briefly Mn_4. The preparation, x-ray structure, and detailed physical characterization have been reported [16]. Mn_4 crystallizes in a hexagonal space group with crystallographic C_3 symmetry. The complex has a distorted cubanelike core geometry and is $Mn^{III}_3Mn^{IV}$. 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 [16].

All measurements were performed using an array of micro-SQUIDs [17]. The high sensitivity allows us to study single crystals of SMMs of the order of 10 to 500 μm. The field can be applied in any direction by separately driving three orthogonal coils.

We first review briefly the single-spin model which is the simplest model describing the spin system of an isolated SMM. The spin Hamiltonian is

$$\mathcal{H}_i = -DS^2_{z,i} + \mathcal{H}_{\text{trans},i} + g\mu_B\mu_0\vec{S}_i \cdot \vec{H}. \qquad (1)$$

$S_{x,i}$, $S_{y,i}$, and $S_{z,i}$ are the components of the spin operator; D is the anisotropy constant defining an Ising type of anisotropy; $\mathcal{H}_{\text{trans},i}$, containing $S_{x,i}$ or $S_{y,i}$ spin operators, gives the transverse anisotropy which is small compared to $DS^2_{z,i}$ in SMMs; and the last term describes the Zeeman energy associated with an applied field $\vec{H}$. The index i labels different SMMs (see below). This Hamiltonian has an energy level spectrum with $(2S + 1)$ values which, to a first approximation, can be labeled by the quantum numbers $m = -S, -(S-1), ..., S$ taking the z axis as the quantization axis. The energy spectrum can be obtained by using standard diagonalization techniques (Fig. 1). At $\vec{H} = 0$, the levels $m = \pm S$ have the lowest energy. When a field H_z is applied, the levels with $m > 0$ decrease in energy, while those with $m < 0$ increase. Therefore,

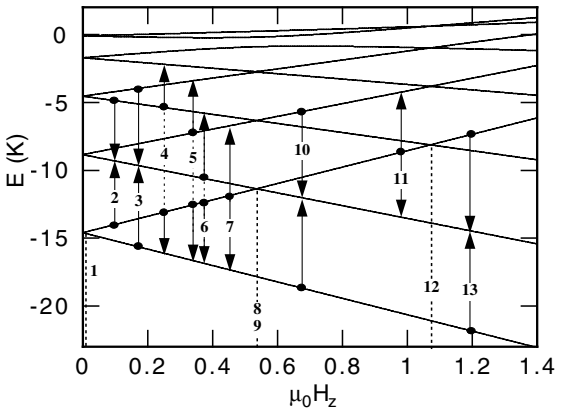

FIG. 1. Zeeman diagram of the ten levels of the $S = 9/2$ manifold of Mn_4 as a function of the field applied along the easy axis [Eq. (1) with $D = 0.72$ K, and a transverse anisotropy term $E(S_x^2 - S_y^2)$ with $E = 0.033$ K [18]]. From bottom to top, the levels are labeled with quantum numbers $m = \pm 9/2,\ \pm 7/2,\ \ldots,\ \pm 1/2$. The levels cross at fields given by $\Delta H_z \approx n \times 0.53$ T, with $n = 1, 2, \ldots$. The arrows, labeled from 1 to 13, indicate two-body tunnel transitions that are given in Table I.

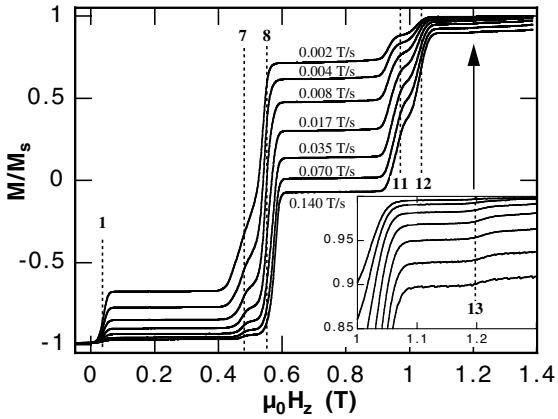

FIG. 2. Hysteresis loop measurements of a single crystal of Mn_4 at low temperatures (40 mK) where thermal activation to excited spin states can be neglected. The field is applied in the direction of the easy axis of magnetization and swept at a constant rate between 0.002 and 0.14 T/s. The tunnel transitions 7, 11, and 13 are SSCR (Table I). Inset: Enlargement for the higher field region.

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 ($\mathcal{H}_{\text{trans}}$), 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 (perpendicular to the S_z direction).

The effect of these avoided level crossings can be seen in hysteresis loop measurements. Figures 2 and 3 show typical hysteresis loops for a single crystal of Mn_4. When the applied field is near an avoided level crossing, the magnetization relaxes faster, yielding steps separated by plateaus. A closer examination of the tunnel transitions, however, shows fine structures which cannot be explained by the above model. We suggest that these additional steps are due to a collective quantum process, called SSCR, involving pairs of SMMs which are coupled by dipolar and/or exchange interactions. We used different techniques to show that different species due to loss of solvent or other defects are not the reason of the observed additional resonance transitions. Such SSCR processes were recently observed in the thermally activated regime of a $LiYF_4$ single crystal doped with Ho ions [19].

In order to obtain an approximate understanding of SSCR, we consider the Hamiltonian describing two coupled SMMs:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + J\vec{S}_1 \cdot \vec{S}_2, \qquad (2)$$

where each SMM is modeled by a giant spin with a spin ground state S and an Ising-like anisotropy; the corresponding Hamiltonian is given by Eq. (1), where $i = 1$ or 2 labels the two SMMs. The two SMMs are coupled by a small exchange interaction J which comprises the contributions of dipole-dipole and/or superexchange interactions [Eq. (2)]. For simplicity, we have assumed isotropic exchange. The $(2S + 1)(2S + 1)$ energy states of the dimer can be calculated by exact diagonalization and are plotted in Fig. 4 as a function of a magnetic field applied along the easy axis of magnetization. Any energy level crossing of such a diagram can be a possible quantum transition depending on the magnitude of transverse terms [Eqs. (1) and (2)] and the type of the transition. We will see that only a few of them are relevant at very low temperatures.

Before proceeding to the detailed discussion of this diagram, it is important to note that, in reality, a SMM is

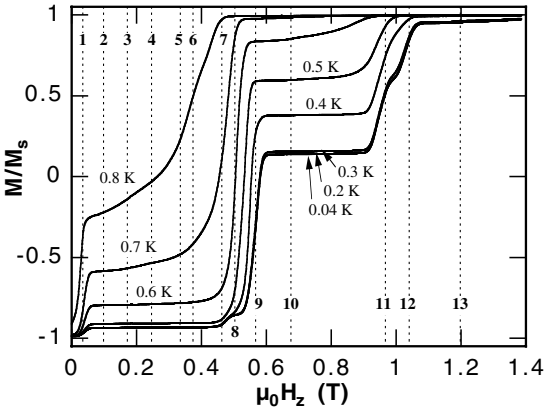

FIG. 3. Hysteresis loop measurements similar to Fig. 2 but at different temperatures and for a field sweep rate of 0.035 T/s. The tunnel transitions are labeled by numbers given in Table I.

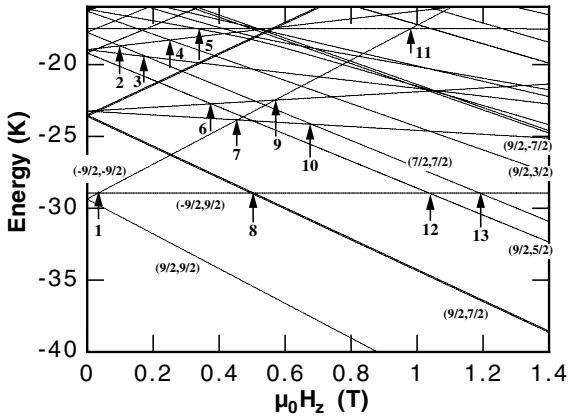

FIG. 4. Low lying energy states of two coupled spins $S = 9/2$, having the same anisotropy as in Fig. 1, as a function of applied magnetic field [Eq. (2) with $J = -0.01$ K]. Arrows, labeled 1 to 13, indicate the observed tunnel resonances given in Table I. Note that most levels are almost degenerated due to the weak exchange interaction.

coupled to many other SMMs which, in turn, are coupled to many other SMMs. This represents a complicated many-body problem leading to quantum processes involving more than two SMMs. However, the more SMMs that are involved, the lower is the probability for occurrence. In the limit of small exchange couplings and transverse terms, we therefore consider only processes involving one or two SMMs. The mutual couplings between all SMMs should lead mainly to broadenings and small shifts of the observed quantum steps.

We measured the interactions between molecules by using relaxation measurements as a function of initial magnetization and the *hole digging* method [17]. We found a fine structure of three in the zero field resonance that is due to the strongest nearest neighbor interactions of about 0.036 T along the c axis of the crystals. This coincides with the shortest Mn-Mn separations of 0.8032 nm between two molecules along the c axis, while the shortest Mn-Mn separations perpendicular to the c axis are 1.6925 nm. We cannot explain the value of 0.036 T by taking into account only dipolar interactions, which should not be larger than about 0.01 T. We believe therefore that small exchange interactions are responsible for the observed value. Indeed, the SMMs are held together by three H bonds C-H-O which are probably responsible for the small exchange interactions.

We selected 13 level crossings (see Figs. 1–4 and Table I) which we divide into different types and into two regimes: (i) the very low-temperature regime (Fig. 2) and (ii) the regime of small thermal activation to the first activated energy levels (Fig. 3). In the former, we can neglect any activation to excited states. Transition 1 corresponds to the ground state (GS) tunneling from $(-9/2, -9/2)$ to $(-9/2, 9/2)$, i.e., one of the two coupled spins reverses. Transitions 8, 9, and 12 correspond to GS to excited state (ES) tunneling. These transitions are identical to those of the single-spin model [Eq. (1)] with the difference that the coupling to neighboring spins leads to field shifts of about 0.036 T.

TABLE I. The 13 tunnel transitions, which are labeled from 1 to 13 in Figs. 1–4, for two coupled SMMs with $S = 9/2$. Their states are labeled by two quantum numbers (m_1, m_2), where $m_i = -9/2, \ -7/2, \ldots, 9/2$. For clarity, degenerate states such as (m, m') and (m', m) are not both listed. IS: initial state; FS: final state; GS: ground state; ES: excited state; SSCR: spin-spin cross relaxation.

n°	IS	FS	Type
1	$(-9/2, -9/2)$	$(-9/2, 9/2)$	GS-GS
2	$(-9/2, 5/2)$	$(7/2, 7/2)$	ES-SSCR
3	$(-5/2, 9/2)$	$(7/2, 7/2)$	ES-SSCR
4	$(-9/2, 5/2)$	$(9/2, 3/2)$	ES-SSCR
5	$(-9/2, -7/2)$	$(9/2, -5/2)$	ES-SSCR
6	$(-9/2, 7/2)$	$(9/2, 5/2)$	ES-SSCR
7	$(-9/2, -9/2)$	$(-7/2, 9/2)$	SSCR
8	$(-9/2, 9/2)$	$(7/2, 9/2)$	GS-ES
9	$(-9/2, -9/2)$	$(-9/2, 7/2)$	GS-ES
10	$(-7/2, 9/2)$	$(7/2, 7/2)$	ES-SSCR
11	$(-9/2, -9/2)$	$(-7/2, 7/2)$	SSCR
12	$(-9/2, 9/2)$	$(5/2, 9/2)$	GS-ES
13	$(-9/2, 9/2)$	$(7/2, 7/2)$	SSCR

Transition 7 is a SSCR wherein a pair of SMMs tunnels from the GS $(-9/2, -9/2)$ to the ES $(-7/2, 9/2)$. That means that this common tunnel transition reverses one of the two spins, and the other makes a transition to an excited state. This excited state is stable only for a short time and relaxes to the GS $(-9/2, 9/2)$. Transition 11 is analogous but from the GS $(-9/2, -9/2)$ to the ES $(-7/2, 7/2)$. Transition 13 is again a SSCR but from the GS $(-9/2, 9/2)$, that is where one spin is already reversed, to the ES $(7/2, 7/2)$.

Transitions 2–6 and 10 are excited state spin-spin cross relaxations (ES-SSCR); that means they reverse from one ES to another ES. For example, transition 10 corresponds to tunneling from $(-7/2, 9/2)$ to $(7/2, 7/2)$.

The SSCR transitions can be seen as virtual phonon transitions. Indeed, whenever there is a field where the energy difference between lower lying energy states is equal to that of higher lying states (see Fig. 1), a transition involving two SMMs can occur provided that both spins are coupled. The transverse terms of the coupling interaction produce a tunnel splitting between two coherently coupled quantum states. When sweeping the field through such a tunnel splitting, there is a Landau-Zener tunnel probability of mutual spin flips: One molecule transfers to a lower energy state, the other to a higher one. The virtual phonon transition picture allows one to immediately locate possible SSCRs in the single-spin Zeeman diagram (see Fig. 1). This method is therefore particularly helpful for large spins where an exact diagonalization

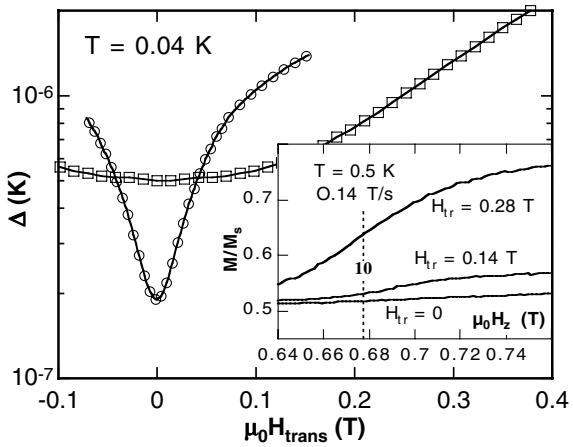

FIG. 5. Tunnel splitting as a function of transverse field for a single molecule transition 1 (circles) and a spin-spin cross relaxation transition 7 (squares). Inset: Enlargement of hysteresis loop measurements at three different transverse fields showing the ES-SSCR transition 10.

of the Hamiltonian matrix of the coupled SMMs is tedious.

We checked that all transitions 1–13 are sensitive to an applied transverse field, which always increases the tunnel rate. The inset of Fig. 5 presents a typical example showing the transverse field dependence of the ES-SSCR transition 10. Figure 5 presents a measurement of the tunnel splitting of transitions 1 and 7 using the Landau-Zener method [8]. The parity of the involved wave function is established by the fact that transition 1 is very sensitive to a transverse field (odd transition), whereas 7 depends only smoothly on the transverse field (even transition) [18]. Indeed, for transition 1 the change of the total quantum number $M = m_1 + m_2$ is odd, whereas it is even for 7.

We calculated all tunnel splittings by numerical diagonalization of Eq. (2) and found tunnel splittings of the right order of magnitude. However, a quantitative comparison is not possible because of the unknown higher order transverse terms [18]. Between transitions 1–13, other avoided level crossings can be found (Fig. 4) that require both SMMs to tunnel simultaneously. The corresponding tunneling probability is very small and will be discussed elsewhere.

In the low-temperature regime, the strongest observed SSCR concerns the transitions 7 and 11. The question arises whether such transitions also play a role in other SMMs such as Fe_8 and Mn_{12}. A diagonalization of the spin Hamiltonian of such molecules shows clearly that SSCR should occur also. However, it turns out that these transitions are very close to the single-spin tunnel transitions and only broaden them. ES-SSCR should, however, be observable and might be responsible for the fine structures seen in experiments of Bokacheva *et al.* [20] on Mn_{12} and of Gaudin [21] and Wernsdorfer [22] on Fe_8.

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[1] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. **115**, 1804 (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. B. Wemple, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. **120**, 839 (1998).
[6] D. J. Price, F. Lionti, R. Ballou, P. T. Wood, and A. K. Powell, Philos. Trans. R. Soc. London A **357**, 3099 (1999).
[7] 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).
[8] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).
[9] A. Garg, Europhys. Lett. **22**, 205 (1993).
[10] J. F. Fernandez and J. J. Alonso, Phys. Rev. B **62**, 53 (2000).
[11] X. Martinez-Hidalgo, E. M. Chudnovsky, and A. Aharony, Europhys. Lett. **55**, 273 (2001).
[12] N. V. Prokofev and P. C. E. Stamp, Phys. Rev. Lett. **80**, 5794 (1998).
[13] W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, and G. Christou, Nature (London) **416**, 406 (2002).
[14] N. Bloembergen *et al.*, Phys. Rev. (Utrecht) **114**, 445 (1959).
[15] M. Lukac, F. W. Otto, and E. L. Hahn, Phys. Rev. A **39**, 1123 (1989).
[16] S. Bhaduri *et al.* (to be published).
[17] W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, and C. Paulsen, Phys. Rev. Lett. **82**, 3903 (1999).
[18] W. Wernsdorfer, S. Bhaduri, C. Boskovic, G. Christou, and D. N. Hendrickson, Phys. Rev. B **65**, 180403 (2002).
[19] R. Giraud, W. Wernsdorfer, A. M. Tkachuk, D. Mailly, and B. Barbara, Phys. Rev. Lett. **87**, 057203 (2001).
[20] L. Bokacheva, A. D. Kent, and M. A. Walters, Phys. Rev. Lett. **85**, 4803 (2000).
[21] G. Gaudin, Ph.D. thesis, Joseph Fourier University, Grenoble, 2001.
[22] W. Wernsdorfer *et al.* (unpublished).