Spin-spin cross-relaxation in single-molecule magnets

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It is shown that dipolar and weak superexchange interactions between the spin systems of single-molecule magnets (SMM) play an important role in the relaxation of magnetization. These interactions can reduce or increase resonant tunneling. At certain external fields, the mechanism of spin-spin cross-relaxation (SSCR) can lead to quantum resonances which can show up in hysteresis loop measurements as well defined steps. A Mn4 SMM is used as a model system to study the SSCR which plays also an important role for other SMMs like Mn12 or Fe8.

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Single-molecule magnets (SMMs)1, 2 are one of the best systems for studying quantum tunneling of large moments3, 4. 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. A molecule straddles the classical/quantum interface in also displaying quantum tunneling of magnetization4, 5, 6, 7, 8, 9, 10 and quantum phase interference11, 12, 13. A quantitative understanding of the mechanism of magnetization tunneling is being developed. For example, the width of tunnel transitions are in general larger than expected from dipolar interactions. Crystal defects may play an important role: loss or disorder of solvent molecules, and even dislocations have been proposed14.

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 non-magnetic atoms in the exchange pathway. Up to now, such an intermolecular exchange interaction has been assumed to be negligibly small. However, our recent studies on several 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 SMMs15.

The main difference between dipole and exchange interactions are: (i) dipole interactions are long range whereas exchange interactions are usually short range; (ii) exchange interactions can be much stronger than dipolar interactions; (iii) whereas the sign of a dipolar interaction can be determined easily, that of exchange depends strongly on electronic details and is very difficult to predict; and (iv) dipolar interactions depend strongly on the spin ground state S, whereas exchange interactions depend strongly on the single-ion spin states. For example, intermolecular dipolar interactions can be neglected for antiferromagnetic SMMs with S = 0, whereas intermolecular exchange interactions can still be important and act as a source of decoherence.

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 not always sufficient to explain the measured tunnel processes. We propose to improve the picture by including also two-body tunnel transitions such as spin-spin cross-relaxation (SSCR)16, 17. 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 [Mn4O3(OSiMe3)(OAc)3(dbm)3], called briefly Mn4. The preparation, X-ray structure, and detailed physical characterization have been reported18. Mn4 crystallizes in a hexagonal space group with crystallographic C3 symmetry. The complex has a trigonal-pyramidal (highly distorted cubane-like) core geometry and is mixed-valent: Mn3III4IV. The C3 axis passes through the MnIV ion and the triply bridging siloxide group. DC and AC magnetic susceptibility measurements indicate a well isolated S = 9/2 ground state19.

All measurements were performed using an array of micro-SQUIDs20. 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

\[ H_i = -DS_{z,i}^2 + H_{\text{trans},i} + g_i \mu_B \mu_0 \vec{S}_i \cdot \vec{H} \]  

where \( S_{x,i}, S_{y,i}, \) and \( S_{z,i} \) are the components of the spin operator; \( D \) is the anisotropy constant defining an Ising type of anisotropy; \( H_{\text{trans},i} \) containing \( S_{x,i} \) or \( S_{y,i} \) spin operators, gives the transverse anisotropy which is small compared to \( DS_{z,i}^2 \) 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 (see 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, 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 $n = 0, 1, 2, 3, ...$

When the spin Hamiltonian contains transverse terms ($H_{\text{trans}}$), 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 $\Delta$, can be tuned by a transverse field (a field applied perpendicular to the $S_z$ direction) via the $S_x H_x$ and $S_y H_y$ Zeeman terms.

The effect of these avoided level crossings can be seen in hysteresis loop measurements. Figs. 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 in the following that these additional steps are due to a collective quantum process, called spin-spin cross-relaxation (SSCR), involving pairs of SMMs which are coupled by dipolar and/or exchange interactions. Such SSCR processes were recently observed in the thermally activated regime of a LiYF$_4$ single crystal doped with Ho ions [21].

In order to obtain an approximate understanding of the spin-spin cross-relaxation, we consider the following Hamiltonian describing two coupled SMMs:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + JS_1 \cdot S_2$$

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 takes into account the contributions of dipole-dipole and/or superexchange interactions (Eq. 2). 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 axes of magnetization. Any energy level crossing of such a diagram can be a possible quantum transition depending on the magnitude of transverse terms and the type of the transition. We will see that only 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 spin of a SMM is 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 of more than two SMMs. However, the more SMMs that are involved, the lower is the probability for its occurrence. In the limit of small exchange couplings and transverse terms we propose therefore to 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 relation measurements as a function of initial magnetization and the hole digging method [19, 21]. 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 co-occurs with the shortest Mn–Mn separations of 8.032 Å between two molecules along the c-axis, while the shortest Mn–Mn separations perpendicular to the c-axis are 16.925 Å. 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 two H bonds C–H–O which are probably responsible for the small exchange interactions.

We selected 13 levels crossings (see Figs. 1 - 4 and Table 1) which we divide into different types and into two regimes: (i) the very low temperature regime and (ii) the regime of small thermal activation to the first activated energy levels. In the very low temperature regime, we
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 direction of the easy axis of magnetization and swept at a constant rate between 0.002 and 0.14 T/s. The tunnel transitions are labeled by numbers, see Table 1. Inset: Enlargement for the higher field region.

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 1.

FIG. 4: The 100 spin state energies 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). Dotted lines, labeled 1 to 13, indicate the observed tunnel resonances given in Tab. 1.

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. The coupling to its neighbor leads to a field shift of about 0.03 T. Transitions 8, 9, and 12, correspond to GS to excited state (ES) tunneling.

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 a 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 a lower lying energy state is equal to that of a higher lying state (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 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. Fig. 5 presents a measurement of the tunnel splitting of transition 1 and transition 7 us-
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). 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 transition 7 depends only smoothly on the transverse field (even transition). Inset: Enlargement of hysteresis loop measurements at three different transverse fields showing the ES-SSCR transition 10.

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 $m_i = -9/2, -7/2, ..., 9/2$. 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) | (9/2,7/2) | 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) | (9/2,5/2) | GS-ES           |
| 13    | (-9/2,9/2) | (7/2,7/2) | SSCR            |

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 like Fe₈ and Mn₁₂. A diagonalization of the spin-Hamiltonian of such molecules shows clearly that spin-spin cross-relaxation should occur. However, it turns out that these transitions are very close to the single spin tunnel transitions and only broaden them. Thermally excited spin-spin cross-relaxation should however be observable and might be responsible for the fine structures seen in experiments of Bokacheva et al. on Mn₁₂ and of Gaudin and Wernsdorfer on Fe₈.

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