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Two-body tunnel transitions in a Mn_4 single-molecule magnet

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Abstract

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.

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Keywords: Single molecule magnets; Quantum tunneling; Exchange bias; Dimer

Single-molecule magnets (SMMs) are one of the best systems for studying quantum tunneling of large moments. 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 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 [1].

In this contribution, 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) which are mediated by dipolar and weak superexchange interactions between molecules [2]. We use here a different Mn_4 SMM to show that at certain external fields SSCRs lead to additional quantum resonances which show up in hysteresis loop measurements as well-defined steps.

The single-crystal X-ray structure of $[Mn_4O_3Cl(O_2CCH_3)_3(dbm)_3]$ has been reported [3,5,6]. It crystallizes in the monoclinic $P2_1/n$ space group with $Z = 4$. The molecule has the trigonal pyramidal $[Mn_3^{III}Mn^{IV}O_3Cl]^{6+}$ core. A virtual C_3 symmetry axis runs through the Mn^{IV} and Cl atoms and defines the magnetic z-axis of each molecule. The four molecules within a unit cell are canted at an angle of 8.97° with respect to one another. DC and AC magnetic susceptibility measurements indicate a well isolated $S = \frac{9}{2}$ ground state [3,5,6].

All measurements were performed using an array of micro-SQUIDs [4]. The high sensitivity allows us to study single crystals of Mn_4.

Fig. 1 shows 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

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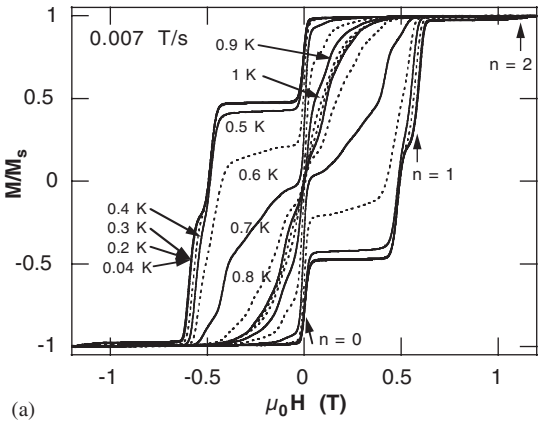

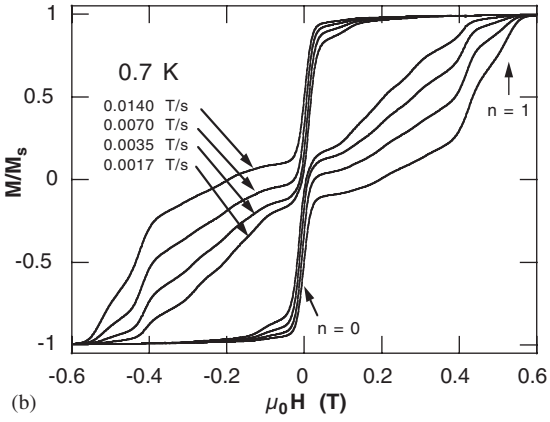

Fig. 1. Normalized magnetization versus applied magnetic field. The resulting hysteresis loops are shown at (a) different temperatures and (b) different field sweep rates. The arrows labelled with $n = 0, 1, 2$ indicate the one-body tunnel transitions. Most of all other steps and kinks are due to two-body tunnel transitions. A quantitative description of the step positions is possible [2].

cannot be explained by the one-body tunnel picture (giant spin 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 [7] and on other Mn_4 SMMs [2].

It is important to note that in reality 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 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.

The question arises whether such transitions also play a role in other SMMs like 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 some of these transitions are very close to the single spin tunnel transitions and only broaden them. Nevertheless, such transitions have been observed and should be included in a quantitative description of the relaxation rates, in particular in the thermally activated regime or for high applied fields.

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