Quantum tunneling in a three-dimensional network of exchange-coupled single-molecule magnets

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A Mn₄ single-molecule magnet is used to show that quantum tunneling of magnetization is not suppressed by moderate three-dimensional exchange coupling between molecules. Instead, it leads to an exchange bias of the quantum resonances which allows precise measurements of the effective exchange coupling that is mainly due to weak intermolecular hydrogen bonds. The magnetization versus applied field was recorded on single crystals of [Mn₄]₂ using an array of micro–superconducting quantum interference devices. The step fine structure was studied via minor hysteresis loops.

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Single-molecule magnets (SMM’s), such as Mn₁₂ - Mn₄ and Fe₈, 1-5 have become model systems to study quantum tunneling of magnetization (QTM). 6-11 These molecules comprise several magnetic ions, with their spins coupled by strong exchange interactions to give a large effective spin. The molecules are regularly assembled in large crystals where often all the molecules have the same orientation. Hence, macroscopic measurements can give direct access to single-molecule properties. Many nonmagnetic atoms surround the magnetic core of each molecule. Exchange interactions between molecules are therefore relatively weak and have been neglected in most studies.

Recently, the study of a dimerized SMM [Mn₄]₂ showed that intermolecular exchange interactions are not negligible. 12 This compound belongs to the [Mn₂O₄Cl₄(O₂CR)₃(py)₃]₂ family, with R = CH₂CH₃ and it will be named in the following as compound 1. The spins of the two Mn₄ molecules are coupled antiferromagnetically. Each molecule acts as a bias on its neighbor, the quantum tunneling resonances thus being shifted with respect to the isolated SMM. In this paper we show that even in three-dimensional networks of exchange-coupled SMM’s, ordering effects do not quench tunneling.

We selected a dimerized SMM [Mn₄]₂, called compound 2. The molecule belongs to the same family as compound 1, however R = CH₃. Because this substituent has a smaller volume than R = CH₂CH₃, molecules are packed slightly closer together. This leads to stronger interdimer interactions, which are negligible in compound 1. The preparation, x-ray structure, and detailed physical characterization have been reported elsewhere. 13,14 Compounds 1 and 2 crystallize in the hexagonal space group R3 (bar) with two Mn₄ molecules per unit cell lying head-to-head on a crystallographic S₆ symmetry axis (Fig. 1). The unit-cell parameters are nearly identical: a = b = c = 13.156 Å and 13.031 Å, α = β = γ = 74.56(3)° and 74.81(2)°, V = 2.06864 nm³ and 2.01593 nm³, respectively for compounds 1 and 2. Each monomer Mn₄ has a ground-state spin S = 9/2. The Mn-Mn distances and the Mn-O-Mn angles are similar and the uniaxial anisotropy constant is expected to be the same for the two dimer systems. These dimers are held together via six C-H···Cl hydrogen bonds between the pyridine (py) rings on one molecule and the Cl ions on the other and one

\[ \mathcal{H} = -D S_z^2 + \mathcal{H}_{\text{trans}} + g \mu_B \mu_0 S \cdot \hat{H}, \]  

(1)

The simplest Hamiltonian describing the spin system of an isolated SMM is
Thus, for compound 1 to negative fields and the absence of the quantum tunneling, the energy gap, the so-called tunnel splitting close to an avoided level crossing. The energy spectrum can be obtained by using standard diagonalization techniques. At the dimer Hamiltonian contains transverse terms, 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, can be tuned by a transverse field acting on the molecule is therefore the sum of the applied field $H_{app}$ and the bias field $H_{bias}$:

$$H_z = H_{app} + H_{bias} = H_{app} + \frac{J}{g \mu_B \mu_0} M_2,$$

where $M_2$ is the quantum number of the neighboring molecule and $J$ is the associated exchange coupling. In the following we explain the hysteresis loops when the field $H_{app}$ is swept from negative to positive values. At low temperature, $M_2$ has two possible values, $M_2 = \pm S = \pm 9/2$. We therefore expect resonant QTM for applied fields $\mu_0 H_{app} = n D/\mu_B \pm M_2 J/g \mu_B$, where $n = 0,1,2, \ldots$. The two possibilities of $M_2$ are represented by two combs in Fig. 2(a). The first comb
(0,1,2) corresponds to \( M_2 = -9/2 \) and the second one \((0',1')\) to \( M_2 = 9/2 \). This model describes all observed quantum transitions in Fig. 2 with two fitting parameters \( D/k_B = -0.72 \) K and \( J/k_B = 0.1 \) K. It neglects co-tunneling and other two-body tunnel transitions having a lower probability of occurrence.12,16

Compound 2 displays hysteresis loops similar to those of compound 1. However, the total exchange coupling is larger for compound 2. The values of \( D/k_B = -0.75 \) K and \( J/k_B = 0.15 \) K were obtained from the field positions of the steps in the hysteresis loops. Another difference between the two compounds is that the hysteresis loops of compound 2 exhibit fine structure that cannot be explained by the dimer model described above.\(^17\)

In order to better analyze this fine structure, minor hysteresis loops were measured \(\text{Figs. 3 and 4} \). First, the sample is saturated in positive field; all the molecules are in the \( M = 1 \) \(9/2\) state. Then the field is decreased. The system approaches the first avoided energy-level crossing at a field value of \( \approx 0.5 \) T. A fraction of the dimers switches from \( 1 \) \(9/2\) to \( 2 \) \(9/2\), and the total magnetization of the system decreases, generating a step in the hysteresis loop. When the magnetization reaches the second plateau \( \approx 0.2 \) T, the field is swept back to positive saturation; the tunneling from \( M = -9/2 \) to \( 9/2 \) is favored via the exited state \( 7/2 \) \(\approx 1 \) T. After this transition the sample reaches positive saturation. The purpose of these minor hysteresis loops is to confirm the fine structure of each transition starting from different initial states.

The tunnel transitions exhibit four equidistant kinks, which we explain by the exchange coupling to the three neighboring dimers.\(^17\) The spins of the three neighboring molecules can be either aligned with the magnetic field or reversed, leading to four different situations: from zero to three reversed neighbors.

The exchange coupling between a molecule and its neighbors acts as a supplementary field bias and shifts further the resonance fields. The total field bias induced by the neighbors and the other \( \text{Mn}_4 \) unit of the dimer can be written as

\[
H_{\text{bias}}^{\text{tot}} = \frac{1}{g \mu_B \mu_0} \left( J M_2 + \sum_{i=1}^{3} J' M'_i \right),
\]

where the first term is the contribution of the intradimer coupling, and \( M'_i \) is the quantum number of the three neighboring dimer molecules \( i \) \[\text{Fig. 1(b)}\].

After positive saturation all the molecules are aligned with the field. The first kink in the hysteresis loop corresponds to the QTM of one molecule in the bias field of its nonreversed neighbors. The resonance is shifted towards negative values by the bias field \( H_{\text{bias}} = 9/(2 g \mu_B \mu_0)(J + 3J') \) [see Eq. (4)]. After this first kink, some molecules now have one reversed neighbor. At the second kink it is this newly created population which tunnels generating molecules with two reversed neighbors. The corresponding field shift is \( H_{\text{bias}} = 9/(2 g \mu_B \mu_0)(J + J') \). The third and the fourth kinks are generated by the QTM of molecules having, respectively, two and three reversed neighbors. The field shift
between two consecutive kinks is $\approx 0.1$ T, corresponding to an interdimer interaction $J' \approx 0.015$ K.

Minor hysteresis loops were measured for different field sweep rates (Fig. 3) and reversal fields (Fig. 4) in order to probe the step heights of the fine structure: the smaller the sweep rate, the higher the resulting kink. This dependence is justified by the Landau-Zener model. The main point to note is that heights of two consecutive kinks are correlated. The second kink height is smaller than the first kink height, the third smaller than the second, and so on. This result is in good agreement with our model leading to the eight combs in Fig. 2(b), giving for the three fitting parameters $D/k_B \approx 0.75$ K, $J/k_B \approx 0.1$ K, and $J'/k_B \approx 0.015$ K.

The above results demonstrate that a three-dimensional network of exchange-coupled SMM’s does not suppress QTM. The intermolecular interactions are strong enough to cause a clear field bias, but too weak to transform the spin network into a classical antiferromagnetic material. This three-dimensional network of exchange-coupled SMM’s demonstrate that the QTM can be controlled using exchange interactions, and opens up new perspectives in the use of supramolecular chemistry to modulate the quantum physics of these molecular nanomagnets.