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Magnetization quantum tunneling and improper rotational symmetry

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ABSTRACT

We examine the magnetization quantum tunneling (MQT) behavior expected for a single-molecule magnet (SMM) with improper rotational symmetry. The simplest possible realization is the $[Ni^{II}(hmp)(dmb)Cl]_4$ cubane complex that crystallizes in the $I41/a$ space group, resulting in S_4 molecular point-group symmetry. A mapping is performed of the energy-level diagram obtained via exact diagonalization of a multi-spin Hamiltonian onto that of a giant-spin model which assumes ferromagnetic coupling and a spin $S = 4$ ground state. The results are compared with a similar analysis for a C_3 symmetric Mn_3 SMM ($S = 6$ ground state). In the even rotational case (Ni_4), the time-reversal invariance associated with the spin–orbit interaction gives rise to a zero-field spin-Hamiltonian that possesses an additional mirror plane perpendicular to the S_4 axis, which is not a symmetry element of the molecular point-group. This conclusion applies quite generally to any molecule with improper rotational symmetry (S_q, with q even), including the more widely studied Mn_{12} SMM. The combined Ni_4 and Mn_3 studies lead to some interesting predictions concerning MQT selection rules in molecules with even versus odd rotational symmetries. We conclude by considering a case with essentially no symmetry at all, by deliberately distorting the high-symmetry Ni_4 molecule. In this case, finite gaps are found at all intersections in the energy-level diagram, indicating a complete absence of MQT selection rules.

1. Introduction

Ever since the initial observation of resonant magnetization quantum tunneling (MQT) in the single-molecule magnet (SMM) Mn_{12}-acetate [1,2], chemists and physicists have worked closely together to devise more-and-more sophisticated molecules and experiments with which to test the fundamental quantum mechanical principles that govern this novel effect. Of particular interest is the influence of molecular symmetry. However, the time-reversal invariance of the spin–orbit (SO) interaction that underlies the MQT phenomenon also plays a crucial role [3,4]. Until recently, the clearest manifestations of symmetry in the quantum relaxation behavior associated with SMMs have involved parity effects seen in quantum (Berry) phase interference measurements, which differ fundamentally for integer- and half-integer-spin states [5], as well as for even and odd MQT resonances [6].

Very recent low-temperature magnetic studies on an exceptionally high-quality C_3-symmetric Mn_3 SMM provided the first example where magnetization relaxation is completely absent (on reasonable timescales) for a resonance that is forbidden on the basis of the spatial symmetries of the molecule [7]. This result motivated subsequent theoretical analysis by the authors of the present study [8,9]. A mapping was performed between a microscopic Hamiltonian and the standard giant spin approximation (GSA) that treats the Mn_3 SMM as a rigid $S = 6$ entity. The microscopic model showed that when the C_2 axes associated with the 2nd-order magneto-anisotropy tensors of the individual Mn^{III} ions are coincident with the molecular C_3 (z-) axis, the coupled zero-field Hamiltonian possesses an artificially high $C_3 \times C_2 \times C_i = C_{6h}$ symmetry; the additional C_i symmetry arises from the time-reversal invariance of the SO interaction, and the C_{6h} symmetry reduces to C_6 upon application of a longitudinal field (parallel to the molecular C_3 axis). In contrast, when the local C_2 axes are tilted away from the molecular C_3 axis (in a way that preserves the molecular C_3 symmetry), the coupled Hamiltonian possesses $C_3 \times C_i = S_6$ symmetry, which reduces to C_3 upon application of a longitudinal field. In other words, the spin Hamiltonian mimics the molecular C_3 symmetry only in the tilted case, a result that is connected with the broken xy-mirror symmetry that exists for the non-tilted case. Another key finding of this work was the demonstration that odd MQT resonances are possible in molecules with odd rotational symmetries (for further explanation, see below and Ref. [8,9]), contrary to some reports in the literature [10].

The Mn_3 results motivated the present study, with the aim of comparing/contrasting the MQT behavior of molecules with even and odd rotational symmetries. We focus here on a tetranuclear

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Ni_4^{II} molecule [4 × (s = 1)] that constitutes the simplest realization of a SMM with S_4 point-group symmetry [11–15]; strictly speaking, one could couple four spin s = ½ ions (e.g., Cu^{II}), but the local 2nd-order zero-field splitting (zfs) anisotropy would be forbidden in such a case. The S_4 symmetry was chosen for two important reasons: (i) it is the same symmetry as the most widely studied, yet far more complex Mn_{12} SMM [9,16]; and (ii) one of the symmetry elements associated with this point group involves an improper rotation, i.e., a 90° rotation about the S_4 axis followed by an inversion (or xy reflection) [17,18]. The latter property contrasts that of the Mn_3 molecule. However, the odd versus even rotational symmetry is also an important factor distinguishing the two cases. The article is organized as follows: the Ni_4 molecule is described in the following section; a discussion of molecular symmetry and MQT selection rules is given in Section 3, followed by a microscopic analysis in Section 4; the influence of molecular disorder is discussed in Section 5; finally, a summary and conclusions is presented in Section 6.

2. The Ni_4 SMM

The [Ni(hmp)(dmb)Cl]$_4$ molecule (henceforth Ni_4 [11,13]) possesses even rotational symmetry. It crystallizes in an $I41/a$ space group without any lattice solvent molecules, resulting in the availability of extremely clean spectroscopic data (e.g., EPR). The structure of the Ni_4 molecule is displayed in Fig. 1. The exchange-coupled Ni_4O_4 core is a slightly distorted cube with the Ni^{II} ions (spin s = 1) located on opposite corners. The distorted cube retains S_4 point-group symmetry, with the S_4-axis indicated in the figure; note that the molecule is invariant to a 90° rotation about the S_4-axis, followed by an inversion through its center (or a reflection about the horizontal mid-plane).

The four Ni^{II} ions couple ferromagnetically, giving rise to a spin S = 4 ground state [11]. EPR studies reveal a sizeable easy-axis-type anisotropy [11–15], suggesting an appreciable barrier to magnetization relaxation (see below and Fig. 2). Unfortunately, Ni_4 also displays extremely fast zero-field MQT because of its relatively small ground state spin value [19]; this is exacerbated by the fact that MQT interactions couple the $m_S = \pm 4$ ground states very efficiently for S_4 symmetry (see below). This leads to a significant reduction in the effective barrier height. While Ni_4 does display a small magnetic hysteresis below 1 K [19], the fast quantum relaxation at zero-field precludes the observation of additional MQT hysteresis steps in finite applied fields, as is the norm for other high symmetry SMMs with larger ground state spin values. However, the simplicity of the Ni_4 molecule (small spin value, high symmetry, simple cubic topology, etc.) makes it a highly attractive model system for gaining useful theoretical insights into the MQT phenomenon. Importantly, Ni_4 possesses the same S_4 molecular point-group symmetry as the widely studied Mn_{12} SMMs [9,16]. Consequently, the conclusions of this study apply equally to Mn_{12}.

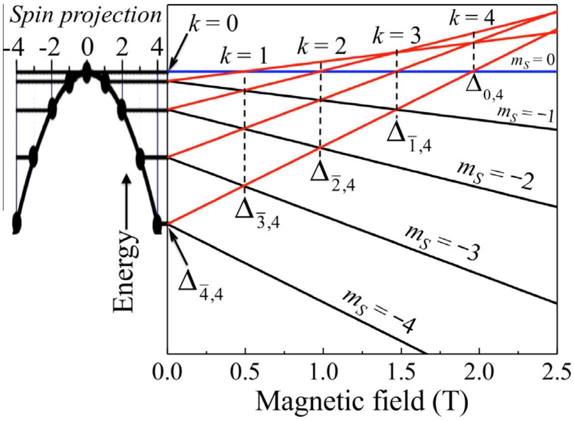

Fig. 2. Zeeman diagram generated for spin S = 4 according to Eq. (1), with $D < 0$ and $H//z$; the zero-field parabolic energy diagram is shown on the left, illustrating the barrier to magnetization relaxation. The energy levels that are most relevant to the pure quantum tunneling regime in Ni_4 have been labeled; the red lines represent states on the metastable ('down') side of the potential barrier, while the black lines correspond to those on the stable ('up') side. The first five level crossings are labeled and also marked with vertical dashed lines, the lowest of which correspond to pure MQT resonances. (Color online.)

3. Molecular symmetry and the giant spin view of MQT

The giant-spin approximation (GSA) has proven extremely useful for describing MQT in SMMs [15]. This approximation completely ignores the internal degrees of freedom within a molecule, treating it instead as a rigid giant spin at low temperatures (S = 4 for Ni_4). The dominant uniaxial SO anisotropy may be captured via a molecular D parameter, giving rise to the following 2nd-order effective spin Hamiltonian, which also includes a Zeeman term:

$$\hat{H}_o = D\hat{S}_z^2 + \mu_o\mu_B\hat{S}\cdot\overleftrightarrow{g}\cdot\boldsymbol{H}. \tag{1}$$

Here, $\hat{S}$ represents the total spin operator, and $\hat{S}_i$ ($i = x, y, z$) its components; μ_o is the vacuum permeability and μ_B the Bohr magneton; finally, $\overleftrightarrow{g}$ represents the molecular Landé g-tensor. Although approximate, Eq. (1) provides a good starting point for explaining

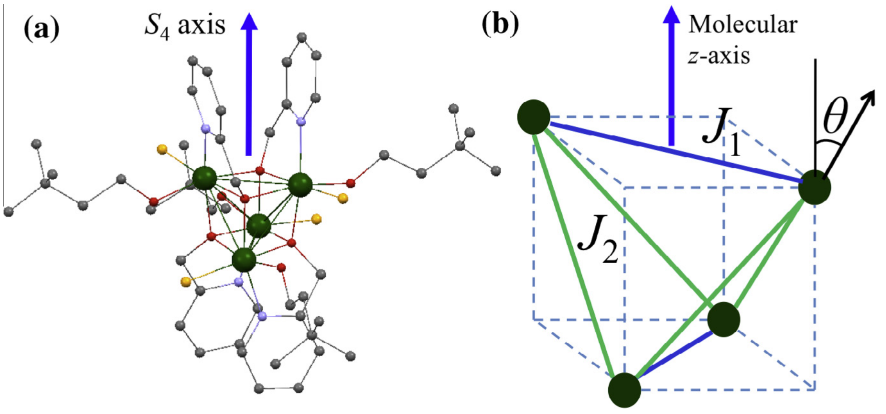

Fig. 1. The structure (a) and schematic representation of the magnetic core (b) of the Ni_4 SMM. Color code: Ni = olive, O = red, N = blue, C = gray and Cl = gold; H-atoms have been omitted for clarity. (Color online.)

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