Polyhedron 66 (2013) 179–182

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Anomalous field sweep rate dependence of the tunnel relaxation in single-molecule magnet Mn_4–Bet

E. del Barco [a,*], K.J. Heroux [b], D.N. Hendrickson [b]

[a] Department of Physics, University of Central Florida, Orlando, FL 32816, USA
[b] Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 92093, USA

ARTICLE INFO

Article history:
Received 31 January 2013
Accepted 1 April 2013
Available online 8 April 2013

Keywords:
Single-molecule magnets
Quantum tunneling

ABSTRACT

We present a low-temperature magnetometry study of the behavior of the quantum tunneling of the magnetization (QTM) in a Mn_4 single-molecule magnet (SMM) as a function of the rate at which a longitudinal magnetic field is swept across a QTM resonance. An initial decrease of the tunnel relaxation rate with increasing field sweeping rate is eventually replaced by an anomalous monotonic increase for moderately high sweep rates. This behavior is distinct from the drastic reversal of the total sample magnetization caused by thermal avalanches ("hot" process), which is commonly observed in other SMMs when increasing the sweep rate, usually due to poor thermal conduction or inadequate thermal anchoring of the sample. We associate the observations to a ("cold") mechanism by which different collections of molecules within the crystal relax collectively without affecting the rest of the molecules.

1. Introduction

It has been two decades since the first observation of magnetic hysteresis in a single-molecule magnet (SMM) [1] and the field has witnessed a tremendous expansion since then, involving a multidisciplinary task-force of researchers around the Globe. Part of this growth is directly related to the exciting potential applications of these systems in current and emerging technologies, including ultra-dense magnetic storage, magneto-cooling or quantum computation, to name a few. Consequently, a substantial amount of fundamental research has been dedicated to gain a proper understanding of the quantum mechanical properties shaping the spin dynamics of SMMs in their solid state form. In this state, each molecule is exposed to the local crystalline environment and potentially affected by coupling to the lattice (phonons) and short- and long-range interactions with neighboring molecules (i.e. exchange and dipolar interactions).

The most significant characteristic of SMMs is that the sample magnetization can be reversed in the absence of thermal energy by tunneling across an anisotropy barrier that separates opposite spin projections and which results from spin–orbit coupling and is responsible of the low temperature magnetic bistability of the system [2] (see also Refs. [3,4]). It is now well understood that the quantum tunneling of the magnetization (QTM) in SMMs is primarily dictated by the corresponding molecular symmetry. It is this symmetry what shapes the anisotropy barrier [5], determines tunneling rates [6] for each resonance, and imposes spin selection rules [7], among others. Indeed, it has been well documented how distortions modifying the molecular symmetry can strongly affect the QTM characteristics of a SMM [8]. However, when considering SMMs in solid state form, the understanding of interactions with the different degrees of freedom within the crystal and their effect on the QTM behavior of the molecules is crucial for an eventual implementation of these systems in technology.

There have been a number of studies of collective magnetic behavior in SMMs. These include reports of molecular entanglement due to exchange interaction between neighboring molecules [9] and long-range ordering caused by dipolar interactions [10,11], among others. Whether directly connected via exchange or dipolar coupling or indirectly coupled through the lattice (phonons), coupled molecules may display collective behavior departing from the QTM characteristics expected from individual SMMs. An example of the latter is the drastic reversal of the total sample magnetization which is often observed in single crystals of SMMs due to uncontrolled thermal avalanches resulting from feedback with phonons generated during the QTM relaxation. Although this effect could be employed for the generation of controlled bursts of phonons and, perhaps, photons (laser) [12], it is usually an inconvenience which needs to be avoided.

In this article we present the observation of an anomalous behavior of the tunneling rate in a QTM resonance of a single crystal of Mn_4 SMMs upon increasing the rate at which the magnetic field is swept across the resonance. Above a certain sweep rate value, the amount of molecules undertaking tunnel reversal across the anisotropy barrier increases when increasing the sweep rate,

* Corresponding author.
E-mail address: delbarco@physics.ucf.edu (E. del Barco).

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http://dx.doi.org/10.1016/j.poly.2013.04.002

contrary to the expectation from the Landau–Zener theory which governs this type of dynamic tunneling event. As we discuss below, this behavior is distinct from that associated to thermal avalanches in that (a) not all the sample magnetization reverses and (b) a small magnetic field (~200 G) applied transverse to the anisotropy axis eliminates the anomaly.

2. Experimental

Low temperature (T = 35–50 mK) magnetometry experiments have been performed to study the QTM relaxation of $[Mn_4(Bet)_4(mdea)_2(mdeaH)_2](BPh_4)_4$, henceforth Mn_4–Bet [13]. Mn_4–Bet possesses a mixed-valent butterfly-type structure (see inset to Fig. 1), with two central Mn^{III} ions (s^{III} = 2) in the body positions and two Mn^{II} ions (s^{II} = 5/2) in the wing positions. Magnetic superexchange interactions mediated through oxygen bridges result in a ground spin state S = 9 at low temperature, although previous QTM and EPR spectroscopy studies showed the presence of low-lying excited states (e.g. S = 8) [14]. This, together with the extremely high quality of single crystals synthesized without solvent molecules, results in a remarkable QTM behavior which shows sophisticated Berry-phase interference (BPI) patterns in the presence of a longitudinal magnetic field (i.e. for resonance numbers $k > 0$). Nonetheless, the results shown in this work are mainly focused on resonance k = 0 for which no longitudinal field is applied. Indeed, although BPI patterns will also be presented in this article, the interest is placed on an independent observation.

3. Results and discussion

Fig 1 shows the half-loops (upward sweep) of the magnetic hysteresis obtained in a single crystal of Mn_4–Bet SMMs at low temperature (T = 35 mK) and at different sweep rates of the applied longitudinal magnetic field (i.e. parallel to the anisotropy axes of the molecules). Three distinct jumps in the magnetization are observed before reaching saturation. These correspond to QTM resonances k = 0 (H_L = 0), k = 1 ($H_L \sim$ 0.2 T) and k = 2 ($H_L \sim$ 0.4 T). The change in magnetization is proportional to the number of molecules that undergo tunneling across the barrier during the crossing

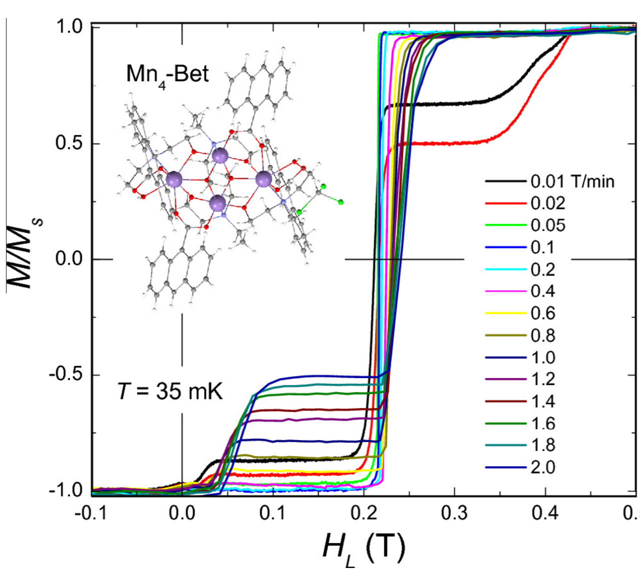

Fig. 1. Up-sweep curves of the magnetization hysteresis loops of a single crystal of Mn_4–Bet SMMs recorded at T = 35 mK as a function of a magnetic field swept at different rates α = 0.01–2.0 T/min along the axial anisotropy axes of the molecules. The inset shows the Mn_4–Bet molecule: Mn(purple), O(red), N(blue), Cl(green), C(gray) and H(white). (Color online)

of a resonance. For rates $\alpha \leqslant 0.02$ T/min (red curve in Fig. 1), the amount by which the magnetization changes decreases with increasing sweep rate.

This is the normal behavior expected from the Landau–Zener theory, which gives the following expression for the tunnel probability in crossing a QTM resonance:

$$P_k = 1 - \exp\left(-\frac{\pi\Delta_k^2}{2g\mu_B(2S-k)}\frac{n}{\alpha}\right) \quad (1)$$

where Δ_k is the tunnel splitting separating the symmetric and antisymmetric superpositions between the crossing levels at resonance k, and n is the number of times the resonance is crossed (in the case of Fig. 1, n = 1 since the resonance is crossed only once in sweeping the field continuously up). The probability can be extracted from the measurements by normalizing the change in magnetization as $P_k = (M_{after} - M_{before})/(M_s - M_{before})$, where Ms is the saturation magnetization and M_{before} and M_{after} are the magnetizations before and after crossing the resonance, respectively.

As can be clearly grasped from Eq. (1), the magnetization jump at a resonance should behave inversely proportional to the sweep rate of the field, which is the case of resonance k = 0 for rates $\alpha \leqslant 0.1$ T/min. However, in resonance k = 1 the total sample magnetization reverses completely for rates above 0.02 T/min. The way this reversal occurs at resonance k = 1 – suddenly and in a field range much shorter than that associated with the field-width of the resonance observed at lower rates – is reminiscent of uncontrolled thermal avalanches which result from an uncontrolled feedback with phonons generated by the first relaxing molecules. These first phonons are absorbed by other molecules which, in turn, will relax and emit more phonons to be absorbed by others molecules, leading to a sequential amplification that results in the total reversal of the sample magnetization. Since phonons promote population of excited spin states in the molecules, this process can also be understood by assuming that the sample is at an effective temperature substantially higher than the experiment temperature. Thus the term *thermal avalanches* is used to describe a "hot" magnetic relaxation process.

The situation is different in resonance k = 0. Here, when increasing the sweep rate above 0.1 T/min, the magnetization starts to increase instead of further decreasing. This is also contrary to the Landau–Zener expectation. However, this anomalous process does not lead to a complete reversal of the magnetization, such as in resonance k = 1 and in many other reports of magnetic thermal avalanches in SMMs. In this case, the magnetization change is finite and the relaxation stops before reaching saturation. In addition, the resonance is not sharp, as is usually the case when thermal avalanches take place. In fact, the field-width of the resonance increases (from ~200 G at $\alpha \leqslant 0.1$ T/min to ~400 G at $\alpha > 0.1$ T/min). This anomalous behavior continues all the way up to the highest sweep rate that can be attained with the superconducting magnet employed (α = 2 T/min). This can be better observed in Fig. 2, where the tunnel probabilities of resonances k = 0 and k = 1 are shown as a function of the field sweep rate. The steady increase of P_0 as a function of α is surprising and, to the authors' knowledge, has not been observed previously in any SMM.

Before discussing the possible scenarios behind the observed anomalous behavior in k = 0, we shall present measurements obtained in the presence of a magnetic field applied transverse to the easy anisotropy axes of the molecules ($H_T > 0$) since small H_T values are capable of making the anomaly completely disappear. Measurements obtained in the presence of a transverse field are performed as follows (see Ref. [13] for further details). First, the sample is saturated with a high negative longitudinal field. Next, a transverse field, H_T, is applied at a given direction within the hard anisotropy plane of the molecules and kept constant while the lon-