Quantum Nucleation in a Single-Chain Magnet

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The field sweep rate \(v = dH/dt\) and temperature \(T\) dependence of the magnetization reversal of a single-chain magnet is studied at low temperatures. As expected for a thermally activated process, the nucleation field \(H_n\) increases with decreasing \(T\) and increasing \(v\). The set of \(H_n(T, v)\) data is analyzed with a model of thermally activated nucleation of magnetization reversal. Below 1 K, \(H_n\) becomes temperature independent but remains strongly sweep rate dependent. In this temperature range, the reversal of the magnetization is induced by a quantum nucleation of a domain wall that then propagates due to the applied field.

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Recent efforts in synthetic chemistry have led to a quickly growing number of magnetic systems that show slow relaxation of magnetization. Apart from interest in applications in, for instance, ultrahigh density magnetic recording, such systems are ideal to test theories. A well-known example is the single-molecule magnet (SMM) that exhibits slow magnetization relaxation of their spin ground state, which is split by axial zero-field splitting [1,2]. SMMs are among the most promising candidates for observing the limits between classical and quantum physics [3]. A more recent example is the single-chain magnet (SCM) [4–6] showing slow relaxation of magnetization as the consequence of the uniaxial anisotropy seen by each spin on the chain and magnetic correlations between spins. Although it seemed that there was a reasonable agreement between the experimental data and Glauber’s theory of a 1D Ising spin chain [7], it was shown that several other arguments should be considered to fill the gap between the theory and the experimental results [8]. The most important arguments concerned the introduction of magnetic anisotropy and finite-size effects. Indeed, their influence on the static and dynamic properties of the SCMs was confirmed experimentally [8–11].

Quantum tunneling of domain walls in a 1D mesoscopic ferromagnetic sample was theoretically investigated [3,12–17] and crossover temperatures between the classical and quantum regime were predicted. Domain wall nucleation and depinning were studied in single Ni wires and showed indeed a flattening of the temperature dependence of the mean switching field \((H_{sw})\) below about 5 K [18] and 1 K [19]. Because of surface roughness and oxidation, the domain walls of a single wire were trapped at pinning centers. The pinning barrier decreases with an increase of the magnetic field. When the barrier is sufficiently small, thermally activated escape of the wall occurs. A flattening of the temperature dependence of \(H_{sw}\) and a saturation of the width of the switching field distribution were observed. The authors proposed that a domain wall escapes from its pinning site by thermal activation at high temperatures and by quantum tunneling below \(T_c \sim 5\) K [18] and 1 K [19]. However, such crossover temperatures are about 3 orders of magnitude higher than the \(T_c\) predicted by current theories [16]. The propagation of a domain wall across an energy barrier in a domain wall junction was also studied and preliminary investigations seems to indicate the possibility of quantum tunneling below 0.7 K [20].

In this Letter, we show that tunneling can occur in truly 1D systems like SCM provided that a driving field is applied that lowers the energy barrier. Indeed in zero applied field, the probability of tunneling is negligible due to the exponential increase of the correlation length.

The studied SCM is a heterometallic chain of \(\text{Mn}^{III}\) and \(\text{Ni}^{II}\) metal ions: \([\text{Mn}_2(\text{saltmen})_2\text{Ni}(\text{pao})_2(\text{py})_2]\)\(\text{ClO}_4\)\(_2\) (saltmen\(^2^-\) = N, N’- (1, 1, 2, 2 - tetramethylethylene) bis(salicylideneiminate); pao = pyridine-2-aldoximate; py = pyridine), called \(\text{Mn}_2\text{Ni}\) chain henceforth [5,9]. At low temperatures, this compound can be described as a chain of ferromagnetic coupled \(S = 3\) \([\text{Mn}^{III}.\text{Ni}^{II}\].\text{Mn}^{III}\)] units.

The spin system of the \(\text{Mn}_2\text{Ni}\) chain can be described by an anisotropic Heisenberg model:

\[
\mathcal{H} = -J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} - D \sum_i S_{iz}^2 - g \mu_B \mu_0 \sum_i \vec{S}_i \cdot \vec{H},
\]

where \(J\) is the ferromagnetic exchange constant between the spin units and \(D\) is the single-ion anisotropy. \(D/k_B = 2.5\) K was obtained from magnetization measurements as a function of a magnetic field applied perpendicular to the easy axis [8]. ac and dc relaxation time measurements showed a unique relaxation time over 10 decades. Above 2.7 K, the thermal dependence of the relaxation time followed an Arrhenius law with an activation energy of 74 K. Below 2.7 K, a departure from this simple behavior was observed and a smaller activation energy of 55 K was found around 2 K [8]. The crossover at about 2.7 K was
showed that the magnetization reversal below 2.7 K is [22–25]. ac and dc relaxation measurements at ~H
ciently low temperatures and at zero field, the energy [8]. The exchange energy
ature where the correlation length equals the chain length [8]. Indeed, the activation energy of the relaxation time should
crease from (4J + D)S² to (2J + D)S² at the temperature and field sweep rate dependences of the co-
thermally activated process, were measured and plotted in Fig. 2. As expected for a
chain displays smooth hysteresis loops which are
strongly temperature and field sweep rate dependent. The temperature and field sweep rate dependences of the co-
 coercive fields (called mean nucleation fields Hₙ henceforth) were measured and plotted in Fig. 2. As expected for a
thermally activated process, Hₙ increases with decreasing temperature T and increasing field sweep rate ν =
/dHᵣ/dt. Furthermore, all our measurements showed an almost logarithmic dependence of Hₙ on the field sweep rate (inset of Fig. 2). Hₙ becomes temperature independent below about 0.5 K.

We analyzed the set of Hₙ(T, ν) data with a model of thermally activated nucleation of magnetization reversal analogous to that of a magnetic single-domain particle [22–25]. ac and dc relaxation measurements at H = 0 showed that the magnetization reversal below 2.7 K is dominated by the ends of the Mn₂Ni chain [8]. At sufficiently low temperatures and at zero field, the energy barrier between the two states of opposite magnetization is much too high to observe a reversal. However, the barrier can be lowered by applying a magnetic field in the opposite direction to that of the chain’s magnetization. When the applied field is close enough to the nucleation field of a domain wall, thermal fluctuations are sufficient to allow the system to overcome the nucleation barrier, and a do-
main wall nucleates. Then, due to the applied field, the magnetization of the entire chain reverse via a domain wall propagation process. The domain wall nucleation can be thermally activated at high temperatures or driven by quantum tunneling at low temperatures [12–17].

This stochastic nucleation process can be studied via the relaxation time method consisting of the measurement of the probability that the magnetization has not reversed after a certain time. In the case of an assembly of identical and isolated spin chains, it corresponds to measurements of the time dependence of magnetization. The probability that the magnetization has not reversed after a time t is given by:

\[ P(t) = e^{-t/\tau} \]  (2)

and \( \tau \) can be expressed by an Arrhenius law of the form:

\[ \tau(T, H) = \tau_0 e^{\Delta E(H)/k_B T} \]  (3)

where \( \Delta E(H) \) is the field dependent nucleation energy barrier and \( \tau_0 \) is a prefactor which is supposed to be a constant. In most cases \( \Delta E(H) \) can be approximated by:

\[ \Delta E(H) = E_0 (1 - h)^{\alpha} \]  (4)

where \( h = H/H_n^0 \), \( H_n^0 \) is the nucleation field at zero tem-
perature, \( E_0 \) is roughly the nucleation barrier height at zero applied field, and \( \alpha \) is a constant of the order of unity [for most cases \( 1.5 \leq \alpha \leq 2 \) [26]].

There are two limiting cases: (i) for \( D \ll J \), the nuclea-
tion energy barrier can be calculated exactly [25,27,28]:

![FIG. 1 (color online). Hysteresis loops for the Mn₂Ni chain at 0.04 and 1.4 K and at several field sweep rates.](image)

![FIG. 2 (color online). The mean nucleation field \( H_n \) for the Mn₂Ni chain as a function of temperature and (inset) field sweep rate.](image)
\[ \Delta E(H) = 2k\sqrt{2\mathcal{J}D}(\tanh R - Rh), \]  
\[ \text{where } R = \text{arccosh}(\sqrt{1/h}) \text{ and } k = 1 \text{ or } 2 \text{ for the nucleation at the ends or insight the chain, respectively. For } h = 0, \text{ this energy is the well-known energy of one or two domain walls, respectively. For } h \to 1, \Delta E(H) \approx 4k/3\sqrt{2\mathcal{J}D}(1 - h)^{3/2}; \text{ (ii) for } J = 0, \text{ the spins are decoupled and we have the case of a Stoner-Wohlfarth particle [29,30] with uniaxial anisotropy. When the field is applied along the easy axis of magnetization, all constants can be determined analytically [22,29]: } \alpha = 2, E_0 = KV, \text{ and the switching field } H_{sw}^0 = 2K/M_s, \text{ where } K \text{ is the uniaxial anisotropy constant, } V \text{ is the particle volume, and } M_s \text{ is the saturation magnetization. For SMMs with dominating uniaxial anisotropy: } \alpha = 2, E_0 = DS^2, \text{ and } H_{sw}^0 = 2DS/g\mu_0\mu_B. \text{ In our case of the Mn}_2\text{Ni chain with } D/k_B = 2.5 \text{ K and } J/k_B = 1.56 \text{ K we are not aware of an analytical expression and propose to use } \alpha = 2 \text{ because of the arguments developed in [26].} \]

In order to study the field dependence of the relaxation time \(\tau(T, H)\) and to obtain the parameters of the model, the decay of magnetization has to be studied at many applied fields \(H\) and temperatures \(T\). This is experimentally very time consuming. A more convenient method for studying the magnetization decay is by ramping the applied field at a given rate and measuring the mean nucleation field \(H_n\), which is the field value to obtain zero magnetization (coercive field). \(H_n\) is then measured as a function of the field sweep rate and temperature (Fig. 2). An analogous procedure [12,31,32] was applied to nanoparticles [33] and recently to SMMs [34]. The mean nucleation field of an assembly of identical noninteracting SCMs is given by [35]:

\[ H_n(T, \nu) = H_n^0\left(1 - \left[\frac{kT}{E_0}\ln\left(\frac{c}{\nu}\right)\right]^{1/\alpha}\right), \]

\[ \text{where the field sweeping rate is given by } \nu = dH_n/dt; H_n^0 \text{ is the nucleation field at zero temperature, and } c \text{ depends on the details of the approximations: } c = H_n^0/k_B T/\left[\tau_0\alpha E_0(1 - H_n/H_n^0)^{\alpha - 1}\right] \text{ in [33], } c' = H_n^0/(E_0/kT)^{1/\alpha}/(\tau_0\alpha) \text{ in [32], and it can be taken constant when the exact value of } \tau_0 \text{ is not needed. We applied the three approximations to nanoparticles [33] and to SMMs [34] and found that the first approximation gives a } \tau_0 \text{ which is closest to that extracted from an Arrhenius plot.} \]

The validity of Eq. (6) was tested by plotting the set of \(H_n(T, \nu)\) values as a function of \([\nu\ln(c/\nu)]^{1/2}\) where \(c = H_n^0/k_B T/\tau_0 E_0(1 - H_n/H_n^0)\). If the underlying model is sufficient, all points should collapse onto one straight line by choosing the proper values for the constant \(\tau_0\). We found that the data of \(H_n(T, \nu)\) with \(T > 1 \text{ K} \) fell on a master curve provided \(\tau_0 = 7.4 \times 10^{-9} \text{ s} \) (Fig. 3).

At lower temperatures, strong deviation from the master curves are observed. In order to investigate the possibility that these low-temperature deviations are due to escape from the metastable potential well by tunneling, a common method for classical models is to replace the real temperature \(T\) by an effective temperature \(T^*\) (see inset) which restores the scaling below 1.1 K.

\[ \text{FIG. 3. (a) Scaling plot of the mean nucleation field } H_n(T, \nu) \text{ for field sweep rates between 0.001 and 0.14 T/s and several temperatures: } 0.04 \text{ K and from } 0.2 \text{ to } 2.6 \text{ K in steps of } 0.1 \text{ K.} \]

\[ \text{(b) Same data of } H_n(T, \nu) \text{ and same scales but the real temperature } T \text{ is replaced by an effective temperature } T^* \text{ (see inset) which restores the scaling below } 1.1 \text{ K.} \]
plotted in Fig. 4. The remaining energy barrier for the tunnel process at 0.04 K is ~20 K for 0.001 T/s; (ii) in case of a distribution of nucleation barriers, different parts of the distribution can be probed by applying the method at different $M$ values; (iv) this method is insensitive to small intermolecular interactions when $H_n$ is much larger than the typical interaction field; and (v) the method can be generalized for 2D and 3D networks of spins.

In conclusion, the presented low-temperature studies of the field driven magnetization reversal of the Mn$_2$Ni SCM suggest for the low-temperature region that the magnetization reversal starts by a quantum nucleation of a domain wall followed by domain wall propagation and reversal of the magnetization. Further studies will concern the application of transverse fields which should enhance the quantum nucleation rate.

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[26] $\alpha = 2$ represents high symmetry cases, while lower symmetry gives $\alpha = 3/2$ [R. H. Victora, Phys. Rev. Lett. 63, 457 (1989)]. In the present case, we have such a high symmetry case because the easy axis of each chain unit is aligned with the chain axis and the applied field.
[34] W. Wernsdorfer et al., cond-mat/0509193 [Phys. Rev. B (to be published)].