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 Mn^{III} and Ni^{II} metal ions: $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$ ($saltmen^{2-}$ = N, N′ − (1, 1, 2, 2 − tetramethylethylene) bis(salicylideneiminate); pao^- = pyridine-2-aldoximate; py = pyridine), called Mn_2Ni chain henceforth [5,9]. At low temperatures, this compound can be described as a chain of ferromagnetic coupled $S = 3$ [Mn^{III}-Ni^{II}-Mn^{III}] units.

The spin system of the Mn_2Ni chain can be described by an anisotropic Heisenberg model:

$$\mathcal{H} = -J\sum_i \vec{S}_i\vec{S}_{i+1} - D\sum_i S_{i,z}^2 - g\mu_B\mu_0\sum_i \vec{S}_i\vec{H}, \quad (1)$$

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

interpreted as the manifestation of finite-size effects [8]. Indeed, the activation energy of the relaxation time should decrease from $(4J + D)S^2$ to $(2J + D)S^2$ at the temperature where the correlation length equals the chain length [8]. The exchange energy $J/k_B = 1.56$ K was found which was in agreement with independent thermodynamical measurements. A saturation of a semilog plot of χT versus $1/T$ was used to estimate the mean chain length of about 100 Mn_2Ni units.

The relaxation rate at $H = 0$ is extremely small below 1.4 K. We applied therefore a magnetic field to study the low-temperature relaxation process. The magnetization measurements were performed by using (i) a magnetometer consisting of several 10×10 μm^2 Hall bars and (ii) an array of micro-SQUIDs [21] on top of which a single crystal of Mn_2Ni was placed, for higher and lower fields than 1.4 T, respectively. The field was aligned with the easy axis of magnetization using the transverse field method [21].

Typical hysteresis loops are presented in Fig. 1. The Mn_2Ni chain displays smooth hysteresis loops which are strongly temperature and field sweep rate dependent. The temperature and field sweep rate dependences of the coercive fields (called mean nucleation fields H_n henceforth) were measured and plotted in Fig. 2. As expected for a thermally activated process, H_n increases with decreasing temperature T and increasing field sweep rate $\upsilon = dH_z/dt$. Furthermore, all our measurements showed an almost logarithmic dependence of H_n on the field sweep rate (inset of Fig. 2). H_n becomes temperature independent below about 0.5 K.

We analyzed the set of $H_n(T, \upsilon)$ 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 $\vec{H} = 0$ showed that the magnetization reversal below 2.7 K is dominated by the ends of the Mn_2Ni 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 domain 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:

$$P(t) = e^{-t/\tau} \tag{2}$$

and τ can be expressed by an Arrhenius law of the form:

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

where $\Delta E(H)$ is the field dependent nucleation energy barrier and τ_0 is a prefactor which is supposed to be a constant. In most cases $\Delta E(H)$ can be approximated by:

$$\Delta E(H) \approx E_0(1 - h)^{\alpha}, \tag{4}$$

where $h = H/H_n^0$, H_n^0 is the nucleation field at zero temperature, E_0 is roughly the nucleation barrier height at zero applied field, and α 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 nucleation energy barrier can be calculated exactly [25,27,28]:

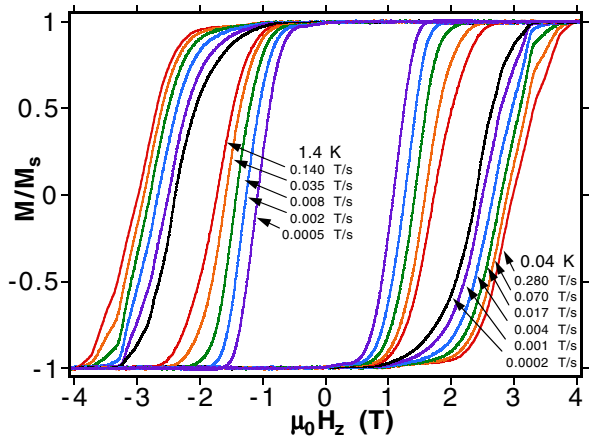

FIG. 1 (color online). Hysteresis loops for the Mn_2Ni chain at 0.04 and 1.4 K and at several field sweep rates.

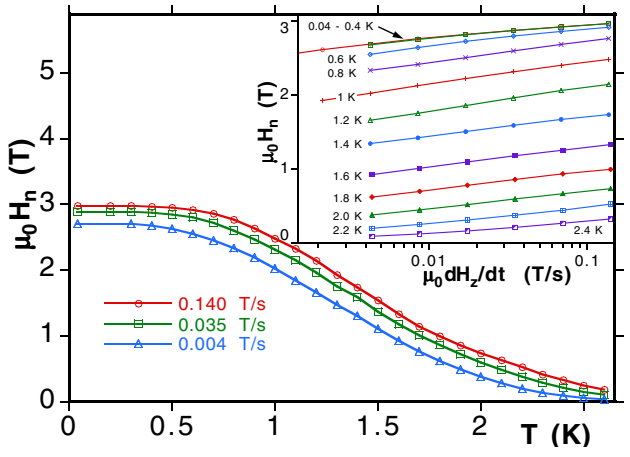

FIG. 2 (color online). The mean nucleation field H_n for the Mn_2Ni chain as a function of temperature and (inset) field sweep rate.

$$\Delta E(H) = 2k\sqrt{2JD}(\tanh R - hR), \quad (5)$$

where $R = \operatorname{arcosh}(\sqrt{1/h})$ and $k = 1$ or 2 for the nucleation at the ends or insight the chain, respectively. For $h = 0$, this energy is the well-known energy of one or two domain walls, respectively. For $h \rightarrow 1$, $\Delta E(H) \approx 4k/3\sqrt{2JD}(1 - h)^{3/2}$; (ii) for $J = 0$, 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]: $\alpha = 2$, $E_0 = KV$, and the switching field $H_{sw}^0 = 2K/M_s$, where K is the uniaxial anisotropy constant, V is the particle volume, and M_s is the saturation magnetization. For SMMs with dominating uniaxial anisotropy: $\alpha = 2$, $E_0 = DS^2$, and $H_{sw}^0 = 2DS/g\mu_0\mu_B$. In our case of the Mn_2Ni chain with $D/k_B = 2.5$ K and $J/k_B = 1.56$ K we are not aware of an analytical expression and propose to use $\alpha = 2$ 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]:

$$H_n(T, \upsilon) \approx H_n^0\left(1 - \left[\frac{kT}{E_0}\ln\left(\frac{c}{\upsilon}\right)\right]^{1/\alpha}\right), \quad (6)$$

where the field sweeping rate is given by $\upsilon = dH_z/dt$; H_n^0 is the nucleation field at zero temperature, and c depends on the details of the approximations: $c = H_n^0 k_B T/[\tau_0 \alpha E_0(1 - H_n/H_c^0)^{\alpha-1}]$ in [33], $c' = H_n^0(E_0/kT)^{1/\alpha}/(\tau_0\alpha)$ in [32], and it can be taken constant when the exact value of τ_0 is not needed. We applied the three approximations to nanoparticles [33] and to SMMs [34] and found that the first approximation gives a τ_0 which is closest to that extracted from an Arrhenius plot.

The validity of Eq. (6) was tested by plotting the set of $H_n(T, \upsilon)$ values as a function of $[Tln(c/\upsilon)]^{1/2}$ where $c = H_n^0 k_B T/\tau_0 2E_0(1 - H_n/H_n^0)$. If the underlying model is sufficient, all points should collapse onto one straight line by choosing the proper values for the constant τ_0. We found that the data of $H_n(T, \upsilon)$ with $T > 1$ K fell on a master curve provided $\tau_0 = 7.4 \times 10^{-9}$ 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

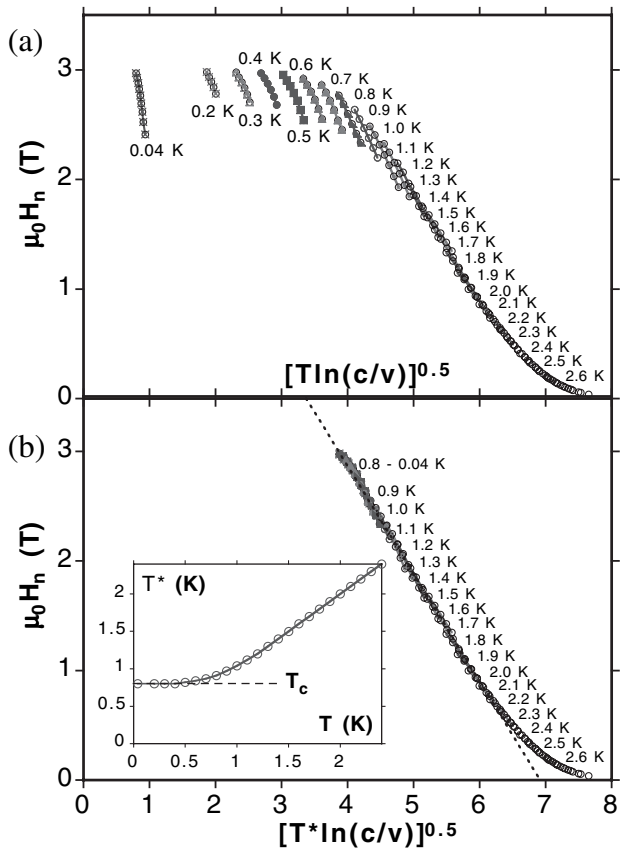

FIG. 3. (a) Scaling plot of the mean nucleation field $H_n(T, \upsilon)$ for field sweep rates between 0.001 and 0.14 T/s and several temperatures: 0.04 K and from 0.2 to 2.6 K in steps of 0.1 K. (b) Same data of $H_n(T, \upsilon)$ and same scales but the real temperature T is replaced by an effective temperature T^* (see inset) which restores the scaling below 1.1 K.

from the metastable potential well by tunneling, a common method for classical models is to replace the real temperature T by an effective temperature $T^*(T)$ in order to restore the scaling plot [3,33,34,36]. In the case of tunneling, $T^*(T)$ should saturate at low temperatures. Indeed, the ansatz of $T^*(T)$, as shown in the inset of Fig. 3(b), can restore unequivocally the scaling plot demonstrated by a straight master curve [Fig. 3(b)]. The flattening of T^* corresponds to a saturation of the escape rate, which is a necessary signature of tunneling. The crossover temperature T_c can be defined as the temperature where the quantum rate equals the thermal one. The inset of Fig. 3(b) gives $T_c = 0.8$ K. The slope and the intercept of the master curves give $E_0/k_B = 47$ K and $\mu_0 H_n^0 = 6.95$ T.

Several points should be mentioned: (i) Eq. (6) is not valid for fields which are close to $H = 0$ because the model only takes into account the nucleation from the metastable to the stable state. However, close to $H = 0$, transitions between both states are possible leading to a rounding of the master curve at small fields; (ii) field dependence of the energy barrier can be obtained directly using [35] and is

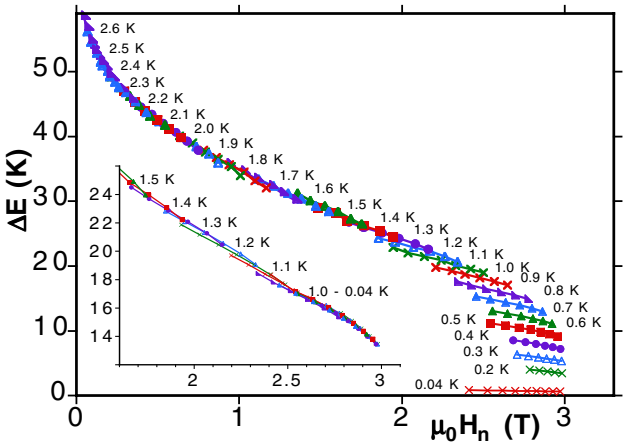

FIG. 4 (color online). Field dependence of the energy barrier of the Mn_2Ni chain obtained from [35] and the set of $H_c(T, \upsilon)$ data from Fig. 3. Inset: same data of $H_c(T, \upsilon)$ but the real temperature T is replaced by an effective temperature T^* [see inset of Fig. 3(b)].

plotted in Fig. 4. The remaining energy barrier for the tunnel process at 0.04 K is ~20 K for 0.001 T/s; (iii) 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_2Ni 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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[35] The probability density of reversal of a stochastic process is $-dP/dt = P/\tau$ and the maximum of the probability density can be derived from $d^2P/dt^2 = P(1 + d\tau/dt)/\tau^2 = 0$. This gives $d\tau/dt = -1$. The application to Eq. (3) leads to $\Delta E(H) = k_B T \ln[k_B T/(\tau_0 \frac{dE}{dH} \frac{dH}{dt})]$. Using Eqs. (4) we find Eq. (6).
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