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 (SCM) 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.

Recent efforts in synthetic chemistry has led to a quickly growing number of magnetic systems that show slow relaxation of magnetization. Apart of interests for 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 exhibit slow magnetization relaxation of their spin ground state, which is split by axial zero-field splitting. SMMs are among the most promising candidates for observing the limits between classical and quantum physics. A more recent example is the single-chain magnet (SCM) 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, it was shown that several other arguments should be considered to fill the gap between the theory and the experimental results. 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.

Quantum tunneling of domain walls in a 1D mesoscopic ferromagnetic sample was theoretically investigated 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 and 1 K. 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. This is a stochastic process that can be characterized by a switching (depinning) field distribution. 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 \( T_c \sim 5 \text{ K} \) and 1 K. However, such crossover temperatures are about three orders of magnitude higher than the \( T_c \) predicted by current theories. 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.

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 MnIII and NiII metal ions: \([\text{Mn}_{2}(\text{saltmen})_{2}\text{Ni}(\text{pao})_{2}(\text{py})_{2})(\text{ClO}_4)_{2}\] (saltmen = \(N,N'-(1,1,2,2\)-tetramethylethylene)bis(salicylideneiminate); pao = pyridine-2-aldoximate; py = pyridine), called Mn2Ni chain henceforth. At low temperatures, this compound can be described as a chain of ferromagnetic coupled \( S = 3 \) \([\text{Mn}^{III}\text{-Ni}^{II}]\) units.

The spin system of the Mn2Ni chain can be described by an anisotropic Heisenberg model:

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

where \( J \) is the ferromagnetic exchange constant between the spin units and \( D \) is the single-ion anisotropy. \( D/k_B = 2.5 \text{ K} \) was obtained from magnetization measurements as a function of a magnetic field applied perpendicular to the easy axis. 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. The crossover at about 2.7 K was interpreted as the manifestation of finite-size effects. 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 \(\xi\). The exchange energy \(J/k_B = 1.56 K\) was found which was in agreement with independent thermodynamical measurements. A saturation of a semi-log plot of \(\chi T\) versus 1/\(T\) was used to estimate the mean chain length of about 100 Mn$_2$Ni 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 \(\times\) 10 \(\mu m^2\) Hall-bars and (ii) an array of micro-SQUIDs on top of which a single crystal of Mn$_2$Ni was placed, for higher and lower fields than 1.4 T, respectively. The field can be applied in any direction by separately driving three orthogonal superconducting coils. The field was aligned with the easy axis of magnetization using the transverse field method.

Typical hysteresis loops are presented in Fig. 1. The Mn$_2$Ni chain displays smooth hysteresis loops which are strongly temperature and field sweep rate dependent. The temperature and field sweep rate dependencies 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 \(v = dH_z/dt\). Furthermore, all our measurements showed an almost logarithmic dependence of \(H_n\) on the field sweep rate (Fig. 2b). \(H_n\) becomes temperature independent below about 0.5 K.

We analyzed the set of \(H_n(T, v)\) data with a model of thermally activated nucleation of magnetization reversal analogous to that of a magnetic single-domain particle. AC and DC relaxation measurements at \(H = 0\) showed that the magnetization reversal below 2.7 K is dominated by the ends of the Mn$_2$Ni chain and the dynamics were described by the generalized Glauber model taking into account chains with finite lengths. 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.

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:

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

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

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

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:

\[
\Delta E(H) \approx E_0 (1 - h)^a
\]
K is the uniaxial anisotropy constant, and the constants can be determined analytically \[23, 30\]: when the field is applied along the easy axis of magnetization, all constants are decoupled and we have the case of a Stoner-Wohlfarth particle \[30, 31\] with uniaxial anisotropy. When the field \(H_n\) is roughly the nucleation barrier height at zero field, and \(H_n^0\) is the nucleation field at zero temperature, and \(c\) depends on the details of the approximations: \[6\] was tested by plotting the set of \(H_n(T, v)\) values as a function of \([T ln(c/v)]^{1/2}\) where \(c = H_n^0 k_B T/\tau_0 E_0(1 - H_n/H_n^0)^{\alpha - 1}\) in the case of the Mn$_2$Ni 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 \[23\].

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 \[13, 32, 33\] was applied to nanoparticles \[34\] and recently to SMMs \[35\].

We applied the three approximations to nanoparticles \[34\] and to SMMs \[35\] and found that the first approximation gives a \(\tau_0\) which is closest to that extracted from an Arrhenius plot.

The validity of Eq. 6 was tested by plotting the set of \(H_n(T, v)\) values as a function of \([T ln(c/v)]^{1/2}\) where \(c = H_n^0 k_B T/\tau_0 E_0(1 - H_n/H_n^0)^{\alpha - 1}\) in the case of the Mn$_2$Ni 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 \[23\].

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The mean nucleation field of an assembly of identical non-interacting SCMs is given by:

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

where the field sweep rate is given by \(v = dH_z/dt\); \(H_n^0\) is the nucleation field at zero temperature, and \(c\) depends on the details of the approximations: \(c = H_n^0 k_B T/\tau_0 E_0(1 - H_n/H_n^0)^{\alpha - 1}\) in \[34\], \(c' = H_n^0 (E_0/kT)^{1/\alpha}/(\tau_0 \alpha)\) in \[32\], and it can be taken constant when the exact value of \(\tau_0\) is not needed.

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ature where the quantum rate equals the thermal one. The inset of Fig. 3b 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) the remaining energy barrier for the tunnel process at 0.04 K can be calculated using Eq. 4. We found \( \sim 30 \) K for a field sweep rate of 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$_2$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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**ANNEX**

The probability density of reversal of a stochastic process is

\[
- \frac{dP}{dt} = \frac{1}{\tau} P
\]  

(7)
and the maximum of the probability density can be derived from
\[ \frac{d^2 P}{dt^2} = \frac{P}{\tau^2} \left( 1 + \frac{d\tau}{dt} \right) = 0 \tag{8} \]
This gives the following general result for the maximum of the probability density
\[ \frac{d\tau}{dt} = -1 \tag{9} \]
The application of the result to Eq. (3) leads to
\[ \Delta E(H) = k_B T \ln \left( \frac{k_B T}{\tau_0} \right) \frac{dE}{dH} \frac{dH}{dt} \tag{10} \]
Using Eqs. (4) and (10), we find Eq. (6).

Eq. (10) can be used to plot directly the field dependence of the energy barrier (Fig. 4).

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