Glauber dynamics in a single-chain magnet: From theory to real systems

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(Received 12 December 2003; published 15 April 2004)

The Glauber dynamics is studied in a single-chain magnet. As predicted, a single relaxation mode of the magnetization is found. Above 2.7 K, the thermally activated relaxation time is mainly governed by the effect of magnetic correlations and the energy barrier experienced by each magnetic unit. This result is in perfect agreement with independent thermodynamical measurements. Below 2.7 K, a crossover towards a relaxation regime is observed that is interpreted as the manifestation of finite-size effects. The temperature dependences of the relaxation time and of the magnetic susceptibility reveal the importance of the boundary conditions.

DOI: 10.1103/PhysRevB.69.132408 PACS number(s): 75.10.Pq, 75.40.Gb, 76.90.+d

The design of new slow-relaxing magnetic nanosystems is a very challenging goal for both applications (as information storage) and fundamental research. A well-known example of such systems is the single-molecule magnet (SMM) that shows slow reversal of the magnetization due to the combined effect of a high-spin ground state and uniaxial anisotropy producing an energy barrier between spin-up and spin-down states.[1] When a magnetic field is initially applied to magnetize this system and then removed, the magnetization decays with a material-inherent relaxation time depending on the temperature. The corresponding relaxation time τ follows an Arrhenius law at high temperatures and the activation energy is equal to the barrier height, being roughly $|D|S^2$, where D is the negative uniaxial anisotropy constant and S is the spin ground state of the molecule. At lower temperatures, τ may saturate when quantum tunneling through the barrier becomes relevant.[2]

Another research route of metastable magnetism has recently been explored with the synthesis of single-chain magnets (SCM's).[3–5] In these materials, the slow relaxation of magnetization is not solely the consequence of the uniaxial anisotropy seen by each spin on the chain but depends also on magnetic correlations. The effect of the short-range order becomes more and more important when the temperature is reduced until a critical point is reached at $T=0$ K for one-dimensional (1D) systems. In fact, the relaxation time is found to be exponentially enhanced at low temperatures in agreement with the pioneer work of Glauber devoted to the dynamics of the 1D Ising model.[6] Although it seems that there is a reasonable agreement between the experimental data and the Glauber's theory,[3–5] we show in this communication that several other arguments should be considered to fill the gap between the theory and the experimental results. First, it should be mentioned that the experimental systems are not strictly Ising-like. In the simplest case, they are rather described by an anisotropic Heisenberg model:

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

where J is the ferromagnetic exchange constant between the spin units and D is the single-ion anisotropy. Second, the relaxation time of each magnetic unit, introduced phenomenologically in Glauber's study, is *a priori* temperature dependent[7] and this argument should also be considered. This question is particularly important if each magnetic unit is by itself a slowly relaxing object. Finally, a real material is never perfect and, as the magnetic correlation length becomes exponentially large at low temperature, even a very small number of defects should deeply affect the magnetic behavior of these one-dimensional systems.[8]

In this Brief Report, we analyze the magnetic relaxation of a 1D system, $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$ ($saltmen^{2-}=N,N'$-(1,1,2,2-tetramethylethylene) bis(salicylideneiminate); pao^-=pyridine-2-aldoximate; py=pyridine), characterized recently (Fig. 1).[4] At low temperature, this compound can be described as a chain of ferromagnetic coupled $S=3$ $[Mn^{III}\text{-}Ni^{II}\text{-}Mn^{III}]$ units. By comparing the relaxation time obtained from ac susceptibility with the one deduced from dc measurements (relaxation as a function of time), we show that a unique relaxation time is found over ten decades. We demonstrate a quantitative agreement between the theory and the experiment when the values of J and D obtained from independent thermodynamical mea-

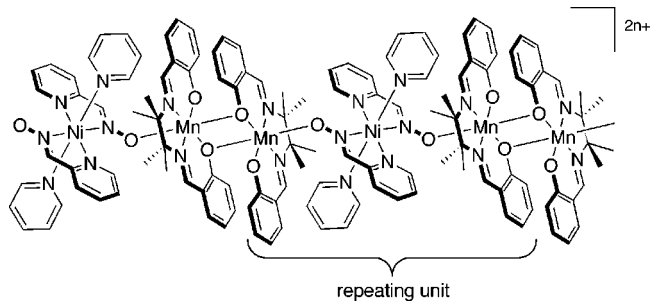

FIG. 1. Schematic view of the chain structure showing the magnetic units (Mn-Ni-Mn trimers) in $[Mn_2(saltmen)_2Ni(pao)_2(py)_2]$ $(ClO_4)_2$ (Ref. 4).

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surements are considered. Moreover we show that finite-size effects should be considered to account for the crossover observed on both the magnetic susceptibility and the relaxation time.

We first present a brief theoretical description of the expected relaxation in a SCM. Critical slowing down of the magnetization is expected in the vicinity of any magnetic critical point. However, the 1D case is singular as only short-range order can be observed at finite temperatures. These correlations affect the dynamic response of the system and a slowing down of the relaxation is expected. The 1D Ising model discussed by Glauber[6] gives a single time process (i.e., a Debye relaxation) with an exponential enhancement of the relaxation time that reads [for a spin state S and with the notations of Eq. (1)]: $\tau(T)=\tau_i(T)\exp(8JS^2/k_BT)$, where $\tau_i(T)$ is the individual relaxation time of each magnetic unit. In this relation, the exponential factor is directly related to the temperature dependence of the correlation functions. At low temperatures, the corresponding energy gap for the correlation length or the magnetic susceptibility is $4JS^2$.[9] For any negative value of D, the correlation length remains exponentially enhanced at low temperatures[10] and we can still expect a Glauber relaxation. The value of the corresponding gap is the energy needed to create a Bloch wall. It remains the same as in the Ising limit as long as $|D|\geqslant 4J/3$.[11] Moreover, each magnetic unit exhibits uniaxial anisotropy which creates a barrier as in the SMM case. For magnetic units with a spin ground state S, we therefore expect $\tau_i(T)$ to vary as $\tau_i(T)=\tau_0\exp(|D|S^2/k_BT)$ when quantum tunneling can be ignored. Finally, we expect the relaxation time to vary as

$$\tau(T)=\tau_0\exp[(8J+|D|)S^2/k_BT]. \tag{2}$$

The second point to consider is the influence of defects along the chain. Finite-size scaling of the Glauber model has been discussed.[12,13] In the case of open chains of size L, a crossover on the relaxation time has been predicted when the magnetic correlation length of the infinite chain, ξ, becomes of the order of L: $\tau_L(\xi)=\tau_\infty(\xi)f_\tau(L/\xi)$ (where the f_τ is the finite-size scaling function introduced in Ref. 12). Following this model, the activation energy of the relaxation time should decrease from $(8J+|D|)S^2$ to $(4J+|D|)S^2$ at the crossover. At approximately the same temperature, we expect a saturation of χT.[9]

The studied SCM is a heterometallic chain of Mn^{III} and Ni^{II} metal ions (Fig. 1). The magnetic unit is a $[Mn^{III}$-Ni^{II}-$Mn^{III}]$ trimer with strong Ni^{II}-Mn^{III} antiferromagnetic interactions ($J_{AF}/k_B=-21$ K).[4] At low temperature ($k_BT\ll J_{AF}$), the trimers can be described as effective $S=3$ units connected within the chains by weaker ferromagnetic interactions (see Fig. 1). The 3D organization of these chains in the solid implies that they can be considered as magnetically isolated. The magnetic susceptibility of this compound becomes anisotropic with almost uniaxial symmetry below 50 K. Between 3.5 K, and 7 K, a frequency dependent ac susceptibility has been systematically observed in both real and imaginary components.[4] It approximately corresponds to a single relaxation time since a satisfactory fit can be obtained using a generalized Debye model with a small α value

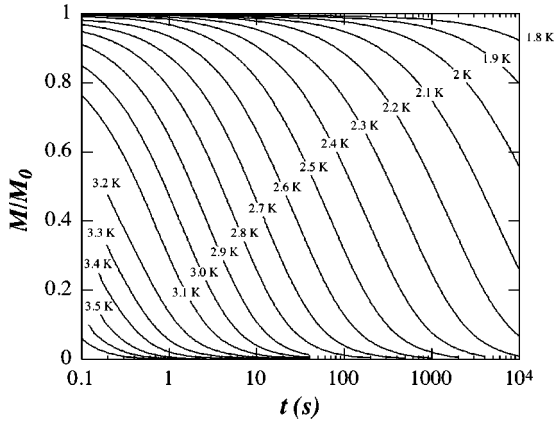

FIG. 2. Relaxation of the normalized magnetization from dc measurements.

(≈ 0.05).[14] Below 3.5 K, the relaxation becomes too slow to be observed from ac susceptibility but dc measurements can still be performed. With this technique, we have been able to follow the relaxation down to 1.8 K, as summarized in Fig. 2. The same shape of the normalized magnetization $m(t)$ is obtained for all the investigated temperatures, i.e., the data can be scaled into a single master curve. As shown in the inset of Fig. 3, a satisfactory fit can be obtained using a stretched exponential, i.e., $m(t)=a\exp[-(t/\tau)^\beta]+b$. The b parameter accounts for a residual slower relaxation which only concerns a small part of the crystal (b is always less than 5% at any temperature). β is always close to 0.8 suggesting that some polydispersity may be present. The deduced relaxation time is depicted in Fig. 3. Note that a consistent value of τ is obtained simply taking the time when the normalized magnetization has reached the value $1/e$. Taken together, ac and dc data show that a crossover is observed around 2.7 K. Indeed, above this temperature the dependence

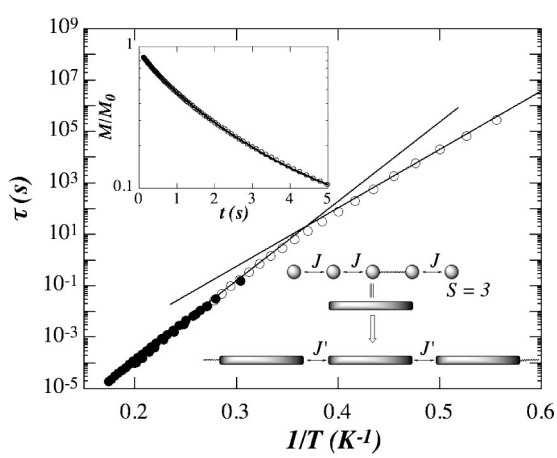

FIG. 3. Semilog plot of the relaxation time τ vs $1/T$. The full and open dots were obtained from ac and dc measurements, respectively. The corresponding straight lines give the energy gaps: $\Delta_1/k_B\approx 74$ K and $\Delta_2/k_B\approx 55$ K. Inset: relaxation of the magnetization at 3 K. Solid line is the best fit obtained with the model defined in the text (top). Schematic view of the magnetic interactions for the model described in the text (bottom).

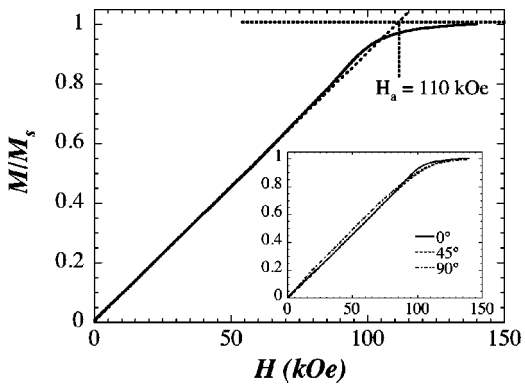

FIG. 4. Field dependence of the magnetization (normalized at the saturation value) when the magnetic field is applied perpendicular to the easy axis at 1.5 K. The intersection between the two dotted lines gives the anisotropy field. Inset: Similar measurements than the main figure at three angles in the plan normal to the easy axis. The main figure is at $\theta=0°$.

of the relaxation time follows an activated law with an activation energy of $\Delta_1/k_B \approx 74$ K. Below 2.7 K, a departure from this simple behavior is observed and a smaller activation energy; $\Delta_2/k_B \approx 55$ K is found around 2 K (see Fig. 3).

Using independent magnetic measurements, we have determined the anisotropy parameter D by measuring the magnetization of a single crystal as a function of a magnetic field applied perpendicular to the easy axis (Fig. 4). We obtain a crossover between a linear dependence of the magnetization at low fields and a saturation at higher fields. Moreover, the data are almost the same for any direction perpendicular to the easy axis (inset of Fig. 4). This behavior is characteristic of the uniaxial anisotropy. An anisotropy field of 110 kOe is deduced from these data which gives $D/k_B = -2.5$ K.[15] The temperature dependence of the magnetic susceptibility is given in Fig. 5 (χT vs $1/T$ in a semilog plot). Full dots were obtained from ac measurements at low frequency (i.e., below the characteristic frequency of the relaxation) with a Quantum Design superconducting quantum interference device

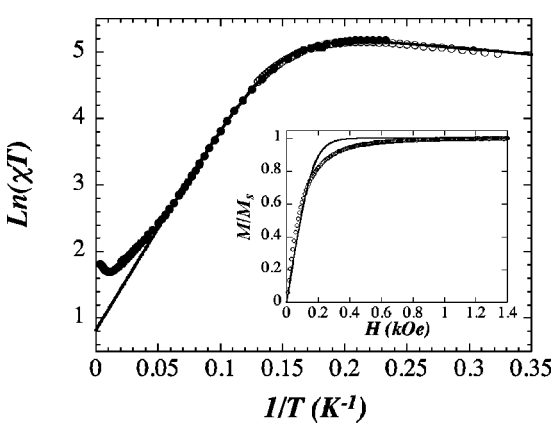

FIG. 5. Semilog plot of χT vs $1/T$ (χ is given in emu/mol). The full and open dots were obtained from ac and dc measurements, respectively. Inset: Field dependence of the magnetization (normalized at the saturation value) at 4 K and with a field sweep rate of 0.14 kOe/s. Solid lines correspond to the fit using the expressions given in Ref. 20.

(SQUID) magnetometer. Open dots were obtained from dc measurements with a micro-SQUID experiment.[16] The expected activated behavior is in fact observed above 6 K (Fig. 5). The deduced gap, $4JS^2/k_B = 28$ K gives an estimation of the exchange energy $J/k_B = 0.78$ K.[17,18] This gives $(8J+|D|)S^2/k_B = 78$ K being in perfect agreement with the activation energy of the relaxation time, Δ_1, measured above 2.7 K [Eq. (2)].

Concerning the low-temperature behavior, χT reaches a maximum around 5 K, while no anomaly was found on the relaxation time. This observation precludes the occurrence of a magnetic phase transition. On the other hand, this result can be explained considering finite-size effects (i.e., the presence of structural defects on the chains which limit the growth of the correlation length). In fact the magnetic susceptibility of a finite Ising chain can be calculated and leads to a saturation of χT at low temperature. To account for the weak decrease of χT observed below 5 K, weak antiferromagnetic interaction, J', can be introduced between finite chains of n spins (as shown in inset of Fig. 3).[19] The corresponding susceptibility can be also determined[20] and gives an excellent agreement to the experimental data below 15 K, where the trimers can be considered as $S=3$ units (Fig. 5). The deduced parameters are the interaction $J'/k_B \approx -47$ mK and the average number of spins between two defects, $n \approx 110$ corresponding to an average distance, $L \approx 140$ nm. A more precise discussion can be made using the field dependence of the magnetization shown at 4 K in the inset of Fig. 5. The same model (solid line, inset of Fig. 5) gives a reasonable fit with $n=90$, in good agreement with the value deduced from the temperature dependence of the susceptibility. As discussed previously, the finite-size effect should also influence the relaxation time and the model of Ref. 13 leads to a crossover at a temperature where the χT product is maximum. In fact, Fig. 3 shows a crossover on the relaxation time, but at a smaller temperature, ≈ 2.7 K, compared to 5 K for the maximum of χT. According to the analysis of the susceptibility measurements, we have generalized the model developed by Luscombe *et al.* taking into account the weak J' interactions.[19] The crossover on the relaxation time now occurs at $k_B T^\star = (4J-4J')S^2/\ln(2n)$, i.e., is shifted at lower temperature for an ferromagnetic interaction, while the activation energy below $T^\star$ becomes $\Delta_2/k_B = (4J+4J'+|D|)S^2$. To obtain $T^\star = 2.7$ K, J'/k_B has to be equal to $+0.37$ K. This value is not in agreement with $J'/k_B = -0.047$ K obtained from the susceptibility. Nevertheless, the activation energy $\Delta_2/k_B \approx 55$ K found around 2 K is close to $(4J+|D|)S^2$ and supports a small J' value.

In summary, the activation energy of a SCM is a combined effect of the individual kinetics of a trimer composing the chain and of the magnetic correlations. The energy parameters J and D deduced from the relaxation time are in excellent agreement with the values independently obtained from magnetic measurements. A crossover is observed at low temperature when the magnetic correlation length becomes of the order of the distance between two defects. A model of these defects in terms of finite-size chains coupled with weaker exchange interactions gives a coherentdescription of

the temperature dependence of the magnetic susceptibility. It also qualitatively explains the temperature dependence of the relaxation time although additional ingredients such as polydispersity on the chain length or exchange interaction may be relevant to improve the discussion of the dynamic properties.

H.M. is grateful for financial support from PRESTO project, Japan Science and Technology Agency (JST). C.C. and R.C. acknowledge the financial support of the CNRS, the Université Bordeaux 1, and the Conseil Régional d'Aquitaine.

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[8] Weak interchain couplings and quantum effects should also be mentioned but will not be considered in the following communication as they remain negligible in the range of temperature presently explored.

[9] In any classical problem, χT (where χ is the magnetic susceptibility) is proportional to the correlation length ξ. Therefore, this result is true for any value of D as long as the spins are considered as classical.

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[11] In this case, these domain walls are localized on one unit cell: B. Barbara, J. Magn. Magn. Mater. **129**, 79 (1994). For smaller values of D/J, the Bloch walls are broader and the gap is a function of D and J. However, Eq. (2) is still valid in this limit as the correlation length remains activated and a Glauber's relaxation is still observable if the corresponding relaxation time belongs to the experimental window.

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[15] The minimization of the sum of the anisotropy and Zeeman energies gives: $2DS^2 = g\mu_B S H_a$, where μ_B is the Bohr magneton. The g factor is close to 2 in the present case.

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[17] In fact, we are in the Ising limit as our estimation of $D/J \approx 3$ is larger than 4/3 (Ref. 12).

[18] This estimation is also in agreement with the mean field analysis of the high-temperature susceptibility (Ref. 4).

[19] The obtained value of J' may be over estimated as antiferromagnetic interchain coupling may also be present. However, this coupling should remain very weak, i.e., negligible, as no magnetic phase transition has been observed above 40 mK.

[20] The expression of the magnetic susceptibility for the model shown in the inset of Fig. 3 is: $\chi = \chi_\infty - \chi_\infty\{1 - \exp[-2n \times \exp(-2K)]\}(1 - \tanh K')/[2n \exp(-2K)\{1 - \tanh K' \exp[-2n \times \exp(-2K)]\}]$, where $\chi_\infty = C \exp(2K)/T$ is the susceptibility of the infinite chain, $K = 2JS^2/k_B T$, $K' = 2J'S^2/k_B T$, and C is the Curie constant for a trimer unit. Below the maximum of χT when $2n \exp(-2K) \ll 1$, this expression reduces to $\chi = nC \exp(2K')/T$. It corresponds to the susceptibility of a chain of weakly coupled (by J') saturated segments of n spins. So, in the same domain of temperatures, the magnetization normalized at its saturation value reads: $m_n = \sinh(ng\mu_B SH/k_B T)/[\sinh^2(ng\mu_B SH/k_B T) + \exp(-4K')]^{1/2}$. This expression has been used to fit the data inset Fig. 5 (solid line).