Glauber slow dynamics of the magnetization in a molecular Ising chain

A. Caneschi,¹ D. Gatteschi,¹ N. Lalioti,¹ C. Sangregorio,¹ R. Sessoli,¹ G. Venturi,² A. Vindigni,² A. Rettori,²,³ M. G. Pini,³ and M. A. Novak⁵

¹ Dipartimento di Chimica, Università degli Studi di Firenze, Via Maraglia 75/77, 50144 Firenze, Italy
² Dipartimento di Fisica, Università degli Studi di Firenze, Largo E. Fermi 2, I-50125 Firenze, Italy
³ Istituto Nazionale per la Fisica della Materia, Unità di Firenze, Largo E. Fermi 2, I-50125 Firenze, Italy
⁴ Istituto di Elettronica Quantistica, Consiglio Nazionale delle Ricerche, Via Panciatichi 56/30, I-50127 Firenze, Italy
⁵ Instituto de Física, Universidade Federal do Rio de Janeiro, CP68528, RJ 21945-970, Brazil

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The slow dynamics (10⁻⁶ s - 10⁵ s) of the magnetization in the paramagnetic phase, predicted by Glauber for 1d Ising ferromagnets, has been observed with ac susceptibility and SQUID magnetometry measurements in a molecular chain comprising alternating Co²⁺ ions and organic radical spins strongly antiferromagnetically coupled. An Arrhenius behavior with activation energy Δ = 152 K has been observed for ten decades of relaxation time and found to be consistent with the Glauber model. We have extended this model to take into account the ferrimagnetic nature of the chain as well as its helicoidal structure.

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Slow magnetic relaxation in low dimensional systems without long range order is a very interesting subject both from the fundamental and the applicative point of view [1]. This phenomenon has been clearly observed and theoretically explained in molecular magnetic clusters, which show also hysteretic effects of molecular origin [2]. These clusters can be considered as magnetic quantum dots, i.e. zero-dimensional compounds. In one-dimensional (1d) systems, a macroscopically slow relaxation was predicted many years ago by Glauber for a ferromagnetic Ising chain. In the last three decades many quasi-1d magnetic compounds were synthesized and characterized and new features were observed, such as nonlinear excitations [3], Haldane gap [4] and spin-Peierls anisotropy, ii) a very high ratio J/J′, between the intrachain and the interchain exchange interactions, leading to a very low critical temperature to three-dimensional (3d) order.

We have recently reported preliminary data which suggest that these conditions can be fulfilled in a real quasi-1d ferrimagnetic compound, [Co(hfac)₂NITPhOMe] (CoPhOMe in the following) [5]. It has a trigonal symmetry with ternary helices [6], along the c axis, formed by Co(hfac)₂ moieties and by the NITPhOMe organic radicals, as outlined in Fig. 1. The primitive cell contains three Co²⁺ metal ions alternating with three radicals. Each Co²⁺ is geometrically related to the other two through a 120° rotation around the c axis and has a local axis of easy anisotropy, z, which makes an angle θ ≃ 50° with c, as observed in monomeric complex of formula Co(hfac)₂(NITPhOMe)₂ [7], where the Cobalt ion coordination is practically the same as in CoPhOMe. The strong 1d character is a consequence of the strong metal-radical magnetic exchange along the chain and of the absence of chemical bond between different chains. The temperature dependence of χT gives a clear indication of 1d behavior, with antiferromagnetic coupling between Co²⁺ and NITPhOMe radical. Since the effective S = 1/2 spin of the Co²⁺ and the S = 1/2 spin of the radical are characterized by different g values (gc and gR in the following), the chains behave as 1d ferrimagnets, due to the non-compensation of the magnetic moments. An approximate quantitative analysis using the alternating spin Ising model suggested that the intrachain exchange interaction is of the order of 200 K in absolute value. The ac magnetic susceptibility shows that the relaxation time of the magnetization below 20 K follows a thermally activated behavior. Below 4 K a stepped hysteresis was observed with the field parallel to the trigonal axis, while no hysteresis was observed with the field perpendicular to c.

We wish to work out here an extension of the Glauber dynamics to a helical Ising ferrimagnet, showing how it can unambiguously justify the experimental features recalled in more detail here below. In Fig. 2 the isothermal magnetization as a function of the field H is reported at T = 2 K for two different orientations of the field. When H is applied along the c axis, a hysteresis cycle appears below 5 K, while the hysteresis is absent down to 2 K for fields applied perpendicularly to c. The unusual shape of the hysteresis (characterized by well defined steps at H = ±4 kOe) is discussed later on. The magnetization, measured by cooling in zero field and then applying a field of 100 Oe, shows the onset of irreversibility around 6 K, if measured with the field parallel to the c axis, while a paramagnetic behavior is observed down to 1.8 K by applying the field in the trigonal plane. The blocking of the magnetization at 6 K is not due to a phase transition to 3d order but has a dynamical nature, as confirmed by ac magnetic susceptibility measurements performed in the range 0.2 Hz - 95 kHz, which show a strong fre-
Another phenomenological parameter, \( \gamma \), of the model. In the case of the tendency of the \( j \)-th spin to align parallel to its nearest neighbors: i.e., the transition probability from the state \( \sigma_j \) to the state \( -\sigma_j \) is assumed to be

\[
w_{\sigma_j \rightarrow -\sigma_j} = \frac{1}{2} \alpha_0 [1 - \frac{1}{2} \gamma_0 (\sigma_j + \sigma_{j+1} - \sigma_{j-1})]
\]

(2)

Imposing the detailed balance it is possible to obtain a correspondence between \( \gamma \) and the exchange constant \( J \) of the Ising model Hamiltonian. When the system has reached equilibrium at temperature \( T \), the ratio of the transition probabilities \( w_{\sigma_j \rightarrow -\sigma_j} \) and \( w_{-\sigma_j \rightarrow \sigma_j} \) must equal the ratio of the Maxwell-Boltzmann probabilities associated with the two equilibrium configurations \( (\sigma_1, \ldots, -\sigma_j, \ldots, \sigma_N) \) and \( (\sigma_1, \ldots, \sigma_j, \ldots, \sigma_N) \).

This yields \( \gamma = \tanh(J/2k_B T) \).

In the Glauber model the direction of each local z axis is determined by the applied field while in our case we will consider as z axis of each Co\(^{2+}\) local axis of easy anisotropy. So inside the same cell we will have three different z axes for the Co\(^{2+}\) ions \((z_1, z_2, z_3)\) and three for the radicals \((z_1, z_3, z_5)\), which are given by the vectorial sum of the directions of magnetic anisotropy of the two Co\(^{2+}\) nearest neighbours). The extended Ising hamiltonian of this system of spins can be written:

\[
\mathcal{H} = -\sum_{n=1}^{N} \sum_{m=1}^{3} \left\{ \frac{1}{2} J (\sigma_{n,2m-1} \sigma_{n,2m}) + \frac{1}{2} \mu_B \left( g_R \sigma_{n,2m-1} \cdot H \cdot \xi_{2m-1} + g_C \sigma_{n,2m} H \cdot \xi_{2m} \right) \right\}
\]

(3)

where \( \xi_j \) is the unitary vector corresponding to the z\(_j\) direction. In the coordinate \( \sigma_{n,j} \), n represents the cell index and \( j \) the magnetic center inside the n-th cell. Since we are interested in the ac response of the sample to an applied oscillating field, we can focus on the stationary solution of the problem. So the system of 6N coupled equations, describing the Markov relaxation process of the spins chain, reduces to six coupled differential equations for the expectation values \( \langle \sigma_{n,j}(t) \rangle \) \((j = 1, \ldots, 6)\). In fact the translational invariance allows to neglect the n index. The equation describing the evolution of the system can be written in matricial form as

\[
\frac{\partial \xi}{\partial (\alpha_0 t)} = A \xi + \bar{\kappa} e^{-i\omega t}
\]

(4)

The \( \bar{\kappa} \) vector depends on the orientation of the oscillating magnetic field with respect to the local axis of each spin and its elements will be specified later on. The symmetric matrix \( A \) has elements \( A_{jj} = -1, A_{j,j+1} = A_{j-1,j} = A_{1,6} = A_{6,1} = \gamma/2 \) and zero otherwise.

Denoting by \( U \) the orthogonal matrix which diagonalizes \( A, D = U \uparrow A U \), we perform the transformations \( \zeta = U^\dagger \xi, \quad \bar{\kappa} = U^\dagger \bar{\kappa} \), so that the system (4) is decoupled as

\[
\frac{\partial \zeta}{\partial (\alpha_0 t)} = D \zeta + \tilde{\kappa} e^{-i\omega t}
\]

(5)
where the diagonal matrix \(D\) has elements \(D_{11} = -1 + \gamma\), \(D_{22} = -1 - \gamma\), \(D_{33} = D_{44} = -1 + \gamma/2\), \(D_{55} = D_{66} = -1 - \gamma/2\). Each equation of the decoupled system (5) can be integrated, in the stationary limit, to give

\[
\zeta_j(t) = \kappa_j \frac{\alpha_j}{\alpha_j - i \omega} e^{-i \omega t}
\]

(6)

with \(\alpha_1 = (1 - \gamma)\alpha_0\); \(\alpha_2 = (1 + \gamma)\alpha_0\); \(\alpha_3 = \alpha_4 = (1 - \gamma/2)\alpha_0\); \(\alpha_5 = \alpha_6 = (1 + \gamma/2)\alpha_0\). Since \(|\gamma| < 1\), we have that \(\alpha_3, \alpha_4, \alpha_5, \alpha_6\) cannot vanish. On the contrary, for \(T \to 0\), \(\alpha_1\) and \(\alpha_2\) can vanish for \(J > 0\) and \(J < 0\) respectively. In our case \(J < 0\) and the slow relaxation (exponentially diverging relaxation time) is expected for \(|J|/k_B T \gg 1\) due to the mode \(\zeta_2\)

\[
\tau_2 = \frac{1}{\alpha_2} = e^{-J/k_B T} 2\alpha_0 \quad \text{(7)}
\]

while \(\tau_1 \simeq 1/\alpha_0\). The law (7) is in agreement with the fit (1) where \(D = -J\) and \(\tau_0 = \frac{1}{2\alpha_0}\).

When the magnetic field is applied along the c axis, its projection along each local axis \(z_j\) is trivially \(H(t) \cos \theta\) and, while \(\kappa_3|| = \kappa_4|| = \kappa_5|| = \kappa_6|| = 0\), one has

\[
\kappa_{2\parallel} = \frac{3}{\sqrt{6}} \frac{\mu_B H_0 S}{k_B T} \frac{1 - \eta^2}{1 + \eta^2} \cos \theta (g_C a - g_R)
\]

(8)

where \(\eta = \tanh \left(\frac{J}{k_B T}\right)\). For \(\kappa_{1\parallel}\) the difference between the Landé factors is substituted by the addition. The complex susceptibility can be obtained through the projection of the contribution coming from each spin:

\[
\chi (\omega) = S^2 \mu_B^2 \cos^2 \theta \frac{N}{k_B T} \frac{1 - \eta^2}{1 + \eta^2} \left\{ \frac{g_C a + g_R}{\alpha_1 - i \omega} + \frac{g_C a - g_R}{\alpha_2 - i \omega} \right\}
\]

(9)

where, since in the experimental conditions (frequency and temperature) \(\omega \ll \alpha_1\), the first term is negligible. Hence, by varying the frequency, \(\chi''\) as a function of \(\chi\) is expected to describe a semicircle, in agreement with the experimental data reported in Fig. 3. If the oscillating magnetic field is applied along a generic perpendicular direction with respect to the c axis, after a few steps we find \(\kappa_{1||} = \kappa_{2||} = 0\) and consequently the slow mode \(\zeta_2\) is not activated but only a linear combination of \(\zeta_3\), \(\zeta_4\), \(\zeta_5\), \(\zeta_6\) is. These results explain the experimental evidence for slow relaxation for magnetic fields applied parallel to the c axis while, for magnetic fields perpendicular to c, the relaxation time \(\tau\) remains of the order of \(\frac{1}{\alpha_0}\).

The hysteresis curves reported in Fig. 2 are characterized by well-defined steps, the more evident observed at \(H = \pm 4\) kOe. The steps observed in the first and third quadrants, i.e. when the magnetization does not change sign, have a static nature, as confirmed by the fact that they are fully reversible (see inset of Fig. 2), do not depend on the sweeping rate of the field, and are observable above the blocking temperature, when the hysteresis disappears. Therefore, their origin seems to be different from the resonant tunneling mechanism observed in molecular magnetic clusters \([14] [17]\). Similar steps of static nature were observed in linear antiferromagnetic chains with alternating magnetic moments when the Zeeman energy is comparable to the exchange interaction \([14]\). In the present case we expect the exchange interaction to be much larger than the Zeeman energy in a field of 4 kOe. However the helical structure and the fact that the local z axes are not pointing along the axis of the helix (\(\theta \simeq 50^\circ\)) can account for this anomaly as well as for the similar saturation values of the two components of the magnetization (Fig. 2) despite the completely different dynamic behavior. This hypothesis has been confirmed by classical transfer matrix calculations and by diagonalization of a finite quantum ring with six spins, where the trigonal symmetry of the helical structure has been taken into account. A detailed description of this study will be the subject of a future publication.

In conclusion, we have shown that CoPhOMe is a quasi-1d ferrimagnetic compound which at low temperature shows slow dynamics of the macroscopic magnetization of the type predicted many years ago by Glauber and never observed before. The presence of magnetic hysteresis in the absence of 3d magnetic order opens the exciting possibility of storing information in an array of magnetic centers with a dramatic reduction in the dimensions (two of the three) of the magnetic memory unit. From a more fundamental point of view, we have extended the theory developed by Glauber for the simple model of an Ising ferrimagnetic chain to the case of helicoidal geometry, and the anomalous dynamic behavior of CoPhOMe turned out to be completely understandable in terms of it.

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[1] D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, Science 265, 1054 (1994).
[2] D. Gatteschi, A. Caneschi, M. A. Novak, R. Sessoli, Nature (London) 365, 141 (1993).
[3] R. J. Glauber, J. Math. Phys. 4, 294 (1963).
[4] H.-J. Mikeska and M. Steiner, Adv. Phys. 40, 191-356.
FIG. 1. Schematic view of the helicoidal structure of CoPhOMe. The laboratory reference frame corresponding to the crystallographic axes \( a^\ast \), \( b \), \( c \) and the local reference frame \((x, y, z)\) are shown. The angle between \( z \) and the \( c \) axis is the \( \theta \) angle mentioned in the text.

FIG. 2. Hysteresis loops recorded on a single crystal of CoPhOMe by applying the field in the \( a^\ast b \) plane (solid line) at \( T = 2 \) K and along the \( c \) axis at 2.0 K (black squares), 3.5 K (open circles) and 4.5 K (open triangles). In the inset: at \( T = 2 \) K the field was cycled three times around the step at 4 kOe. The curves taken with increasing field (solid circles) and decreasing field (solid line) are superimposable, denoting the reversible character of the step.

FIG. 3. Temperature dependence of the imaginary component of the ac magnetic susceptibility measured in zero static field and with the dynamic field oscillating parallel to the \( c \) axis for nine selected frequencies in the range 0.18 Hz - 95 kHz. In the inset \( \chi'' vs \chi' \) (i.e, the Cole-Cole plot) measured at 10 K.

FIG. 4. Temperature dependence of the relaxation time. The data represented by circles have been obtained from the curves of Fig. 3 by assuming that, at the temperature of the maximum in each curve, \( \tau = 1/(2\pi\nu) \), where \( \nu \) is the frequency of the oscillating field. The triangles represent the relaxation time obtained from the decay of the magnetization after having applied and removed a weak field. The solid line represents the fit of the \( \chi'' \) ac data using Eq. (1). The best fit parameters are \( \Delta = 152(\pm 1) \) K and \( \tau_0 = 4(\pm 1)10^{-11} \) s.
Figure 1
Figure 2
Figure 3
Figure 4