DISENTANGLING BETWEEN STATIC AND KINETIC EFFECTS IN THE Hysteresis OF SPIN CROSSOVER MOLECULAR MAGNETS

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Abstract. We investigate the kinetic hysteresis of spin crossover molecular magnets, with the aim of unravelling the link between static and dynamical effects observed in the first order reversal curves (FORC) diagrams. Using a mean-field model, we establish how the FORCs distributions are influenced by both the kinetic effects and the physical parameters of the system.

Key words: kinetic hysteresis, spin crossover molecular magnets, FORC method.
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1. INTRODUCTION

Most of experimental hysteresis loops are quasistatic, as the lifetime of the metastable state is much longer than the usual experimental timescale [1]. However, in some systems, either nanometric or nanostructured, the energy barrier separating the stable and metastable states is small enough so that the relaxation time towards the stable state is on the order of magnitude of the experimental timescale. In this case, the hysteresis width and shape depend on the scan-rate of the input parameter [2, 3].

The physical properties of systems with hysteresis, either ferromagnetic, ferroelectric, elastic or thermal, have been better understood in the last years due to the first order reversal curves (FORC) method, based on the analysis of minor hysteresis loops [4–7]. However, most of the effort in this direction has been devoted only to rate-independent phenomena, mainly due to large experimental costs and time needed to obtain major and minor hysteresis loops with a significant variation in function of the scan rate of the input parameter [8]. Studies of rate-dependent phenomena are nevertheless increasingly important due to the continuous miniaturization of electronic components which is accompanied by a dramatic growth of kinetic effects [9]. In the case of static hysteresis, the FORC distributions can be easily correlated to the presence of domains inside the material and with distributions of biases and coercivities or inter- and intra-domains interactions. In out-of-equilibrium systems, the intrinsic properties can be hindered by the kinetic
effects which induce the deformation and the broadening of the FORC distributions [10, 11].

In this paper, we evaluate the possibility of disentangling between static and kinetic features of FORCs distributions, in the framework of a mean-field model applied to spin crossover (SC) molecular magnets. These systems are prototypes for the study of kinetics FORCs as, if the intermolecular interactions are large enough, they present both static and kinetic hysteresis, following the variation of one single input parameter which is the temperature (Fig. 1). The two electronic states in thermodynamic competition are the diamagnetic low spin state (LS), stable at low temperatures and the paramagnetic high spin state (HS), stable at high temperatures. A hysteresis loop, called the thermal hysteresis (TH), can be detected when temperature is cycled between two extreme values. The relevant macroscopic parameter for the quantitative analysis is the proportion of HS molecules in the system i.e., HS fraction – denoted here as $n_{HS}$. Moreover, by irradiating the sample at low temperature with a light of an appropriate wavelength, one can induce the switching of the LS stable state towards the metastable HS state. The competition between the constant irradiation and the thermal activated HS-LS relaxation, faster with the increasing temperature is at the base of the so-called light induced thermal hysteresis (LITH). In this way, while keeping a constant light irradiation and varying the temperature both TH and LITH can be experimentally obtained in the same series of measurements [12].

![Fig. 1 – Experimental data obtained by magnetometry for Fe(bbr)$_2$(ClO$_4$)$_2$ SC magnet showing TH and LITH with two temperatures sweeping rates (1 K/min: full circles; 0.3 K/min: open circles). The TH loops are superimposed for the two rates (adapted from Ref. [12]).](image)

At low temperatures where LITH is obtained, the relaxation is within minutes, e.g. the order of magnitude of experimental timescale, so LITH is highly affected by the temperature sweeping rate, while nanoseconds relaxation, at higher temperatures, much faster than the experimental timescale leads to a quasistatic thermal hysteresis.

Using the FORC method for TH, it is possible to obtain relevant information on the intrinsic properties of the molecular compounds, such as the bias and the coercivity.
distributions of like-spin domains [10, 13, 14]. In the case of LITH, relevant parameters are the cooperativity factor and the activation energy distribution [15].

Here, we use the FORC method not only to infer the domains distribution, but also to disentangle between kinetic and static components of the LITH and to identify how the distributions of relevant parameters are affected by the kinetics.

2. MODEL AND RESULTS

The FORC method is used to investigate the hysteresis loops, being a successful tool for the exploration of the processes inside the hysteresis loop and showing the distribution of the interaction and the coercive fields. To obtain FORCs for the cooling branch of LITH or TH, the measurements/simulations have to begin from a temperature high enough to ensure that all the molecules are in the stable state. Then, the temperature $T_A$ is decreased in steps of temperature (according to the sweeping rate) until it gets to a specific reversal temperature, $T_B$, at which point it starts to increase again. The process is repeated for different reversal temperatures, $T_B$. The procedure is similar for FORCs starting from heating branch, but for the sake of simplicity in the following we only refer to FORCs starting from cooling branch.

Next, by plotting the second order mixed derivative of HS fraction with respect to the sweeping temperature $T_A$ and the reversal temperature $T_B$, one obtains the FORC diagrams:

$$\rho(T_A, T_B) = -\frac{\partial^2 n_{HS}}{\partial T_A \partial T_B}.$$  \hspace{1cm} (1)

In Fig. 2, we show FORC diagrams for both TH and LITH. In the case of the static TH hysteresis, we can observe a single distribution which can be straightforward connected to distributions of bias and coercivities in the system, by translating the $T_A$, $T_B$ axis system into $(T_A + T_B)/2$ (which correspond to bias) and $(T_A - T_B)/2$ (standing for coercivity) coordinates. In the case of kinetic LITH, two distributions can be identified: one static in the lower part of the figure and another one kinetic along the first bisector which includes also irreversible component. The origin of this negative distribution is due to the continuous evolution of the system toward the stable state, even after the direction of variation of temperature has changed. In addition, even the static component of the distribution has an elongated form, due to the same kinetic effects, which makes the interpretation of the LITH FORC diagram in terms of real physical parameters in the system non-trivial.

Therefore, in the following we intend to correlate the kinetic distributions obtained by the FORC analysis to some distributions of cooperativity parameters and
activation energies by using the classical master equation in the mean field approximation to simulate major and minor hysteresis loops of the kinetic LITH hysteresis.

Fig. 2 – Experimental FORC curves and FORC distribution in the case of TH (top) and LITH (bottom) for Fe(bbtr)2(ClO4)2 molecular magnet.

In the mean field approach, the behavior of complex stochastic models is studied by approximating a large number of small individual components that interact with each other in the lattice, with a single averaged interaction, reducing a many-body problem to a one-body problem. Thus, the intermolecular interaction parameter is identical for every molecule and is equal to an average interaction with all the other molecules in the system. However, the real physical systems respond differently to the temperature variation, because of its multi-domain structure and to the interactions between the domains and with the environment. Thus, the output of the entire system under the temperature sweeping rate is the average output of all the components of the system.

The master equation includes both the irradiation and the HS-LS and LS-HS non-radiative relaxations processes:

\[
\frac{dn_{HS}}{dt} = I_o \sigma (1 - n_{HS}(t)) - k_{HL}(T, n_{HS}) n_{LS}(t) + k_{LH}(T, n_{LS}) (1 - n_{HS}(t)),
\]

where \( I_o \) is the irradiation intensity, \( \sigma \) represents the cross-section of the light absorption, \( k_{HL} \) and \( k_{LH} \) are the HS-LS and LS-HS transitions rates.
In equation (2), the last two terms correspond to the HS-LS and LS-HS non-radiative relaxations processes, respectively. For TH the irradiation term is small enough to be neglected, while at low temperature the LS-HS relaxation is negligible. Therefore, LITH is modelled by the first two terms of the above equation, which can be transformed by explicitly writing the transition rates:

$$\frac{dn_{HS}}{dt} = I_0 \sigma (1 - n_{HS}) - k_{HH} \exp \left( - \frac{E + \alpha n_{HS} T}{k_B T} \right) n_{HS},$$

where $E$ is the activation energy, $\alpha$ is the cooperativity parameter, responsible for interactions inside the system and $k_{HH}^\infty$ is the relaxation rate at a very high temperature.

As in powdered spin crossover materials the micrometric grains are of different sizes, thus resulting in different biases and coercivities of every grain, we have to consider in Eq. (3) appropriate distributions of material intrinsic parameters ($E$ and $\alpha$). The straight way to mitigate this aspect is to consider a multivariate normal non correlated distribution given by the equation:

$$P(E, \alpha) = \frac{1}{2\pi \sigma_E \sigma_\alpha} \exp \left( - \frac{1}{2} \left( \frac{E - E_0}{\sigma_E} + \frac{\alpha - \alpha_0}{\sigma_\alpha} \right)^2 \right),$$

where $P(E, \alpha)$ is the probability density function of $E$ and $\alpha$, $\sigma_E$ and $\sigma_\alpha$ are their standard deviations, $E_0$ and $\alpha_0$ are the average values, respectively. An example of this multivariate distribution is visible in Fig. 3.

Using Eq. (3) with the distribution given by Eq. (4), the dynamic LITH have been simulated by a Runge-Kutta type approach (considering an additional
differential equation of the temperature variation $dT/dt = c$, where $c$ is the temperature sweeping rate), while the static LITH have been obtained by averaging the results given for every point in the distribution by a bisection method when $dn_{LITH}/dt = 0$.

In Fig. 4, we present simulations of the LITH curves, and corresponding FORC distributions for the dynamic and static LITH with the parameters: $k_{HS} = 1 \text{s}^{-1}$, the light irradiation $I_0 \sigma = 10^{-3} \text{s}^{-1}$, $E_0 = 550 \text{K}$, $\sigma_E = 60 \text{K}$, $\alpha_0 = 6$, $\sigma_a = 0.5$.

As expected, the dynamic hysteresis curve simulated for different values of the temperature sweeping rate $c$ becomes narrower as $c$ decreases, resulting in a large dependence of the hysteresis on the temperature sweeping rate.

By overlapping the static LITH into the dynamic LITH one can notice that regardless the value of the temperature sweeping rate $c$, the static hysteresis is included into the kinetic ones. In other words, the kinetic hysteresis approaches the quasistatic hysteresis if the temperature sweeping rate is infinitely small.

The analysis of the FORC distributions brings some interesting results. In Fig. 5, we have represented the difference between the diagrams of the kinetic and static LITH curves, which corresponds practically to the kinetic contribution in FORC diagrams. We notice that the kinetic part is not concentrated just along the first
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bisector, but also in the vicinity of the main static distribution. This suggests that the presumed static distribution is affected itself by the kinetics of the system.

Fig. 5 – Static and dynamic LITH FORCs – curves and the difference between the distributions in the two representation coordinates.

As a consequence, we cannot obtain direct information on the distribution of input parameters $E$ and $\alpha$ from the FORCs experimental distributions affected by kinetics. In order to clarify this point, we propose here a reverse method consisting in correlating the a priori known distributions of input parameters to distributions of $(T_A + T_H)/2$ and $(T_A - T_H)/2$.

Fig. 6 – Example of bias and coercivity distributions: simulations (open circles) and fit (line).

The procedure is the following: (i) from the FORC diagrams represented in the coordinates system $(T_A + T_H)/2$ (bias) and (coercivity) $(T_A - T_H)/2$, for each value of the intrinsic standard deviation parameters ($\sigma_\alpha$ and $\sigma_E$), we find the point of maximum intensity $M$; (ii) we determine the bias distribution around the point $M$ holding the coercivity constant; (iii) we determine the coercivity distribution around the point $M$ holding the bias distribution constant, for that peak intensity point; (iv) both distributions are then fitted by a the Gaussian function given by
equation \( y = y_0 + A \cdot \exp \left( -\frac{1}{2} \left( \frac{x-x_c}{w} \right)^2 \right) \) in order to find the standard deviations of FORC distributions. Examples of such distributions are given in Fig. 6.

Using the data from the Gaussian fits for several input parameters \((\alpha, E, c)\), we have explored how the input parameters and their standard deviations influence the bias and coercivity in the kinetic FORC distributions and their standard deviations as a function of the temperature sweeping rate \(c\). We explore these relationships in Fig. 7. The interaction parameter \((\alpha)\) mainly influences the hysteresis width i.e., \((T_A - T_B) / 2\), while a larger standard deviation \(\sigma_\alpha\) results in a larger \(\sigma_{(T_A - T_B) / 2}\).

However, the most dramatic effect on standard deviation of the coercivity is produced by the temperature sweeping rate \(c\). A large sweeping rate and a small initial \(\sigma_\alpha\) results in a larger \(\sigma_{(T_A - T_B) / 2}\) than a small sweeping rate and a large initial \(\sigma_\alpha\). The situation is slightly different in the case of the activation energy. It influences mainly the hysteresis width i.e., \((T_A + T_B) / 2\), and a larger standard deviation \(\sigma_E\) implies a larger coercivity standard deviation \(\sigma_{(T_A + T_B) / 2}\). In this case the influence of the temperature sweeping rate \(c\) on \(\sigma_{(T_A + T_B) / 2}\) is marginal. On the other side, the temperature sweeping rate has a negligible influence on bias distributions, but an important one for the coercivity distributions. This is due to the fact that the hysteresis width increases with \(c\), but, in a first approximation the middle of the hysteresis does not change its position with \(c\).

![Fig. 7 – Standard deviations of bias and coercivities as reflected in FORC diagrams as a function of standard deviations of the input parameters.](image)
Another aspect can be observed when FORCs are simulated considering a waiting time at the reversal temperature $T_B$. As already mentioned, at $T_B$, the system relaxes to approach the steady state point. As this relaxation time is inherent in experimental data it is instructive to compare the simulation of LITH FORCs and corresponding distributions with and without relaxation time in $T_B$. As we can notice from Fig. 8, an additional waiting time at $T_B$ results in decreasing kinetic effects in FORC diagrams. These results suggest that, in order to have less kinetic effects on FORC diagrams, one should wait more time at the reversal temperature.

![Graph](image)

Fig. 8 – FORCs with and without additional waiting time at reversal points, using the $\sigma = 10^{-5}$ light irradiation $I_0\sigma = 10^{-5}$ s$^{-1}$, $E_0 = 550$ K, $\sigma_E = 60$ K, $\alpha_0 = 6$, $\sigma_0 = 0.8$.

3. CONCLUSIONS

This paper is focused on the mean-field analysis of the static and kinetic hysteresis curves of spin crossover compounds, the interpretation of the first order reverse curves diagrams obtained using the FORC method and the possibility to correlate the kinetic distributions to the intrinsic physical parameters of the systems.

After observing that the static hysteresis and FORC diagrams fits perfectly, in the dynamic one we have obtained linear correlations between the FORC distribution parameters (coercivities and biases) and this intrinsic parameters distributions of (cooperativity parameter and activation energy) with the slope depending on the sweeping rate of the temperature. We concluded that the interaction distribution influences the width of the hysteresis and the coercivity distribution, while the activation energy influences the central transition temperature, related to the bias distribution.

We also noticed that a larger waiting time at the reversal points results unexpectedly in smaller kinetics features of kinetic FORCs, which is an useful finding for experimentalists, as the magnetometry technique present inherently a delay in reversing temperatures [16].
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