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Unified dynamical description of pulsed magnetic field and pressure effects on the spin crossover phenomenon

Sébastien Bonhommeau,^{1,2} Gábor Molnár,¹ Michel Goiran,³ Kamel Boukheddaden,^{4,*} and Azzedine Bousseksou^{1,†}

¹Laboratoire de Chimie de Coordination, UPR 8241 CNRS, 205 route de Narbonne, F-31077 Toulouse Cedex, France

²Laboratoire de Physique des Solides de Toulouse, UMR 5477 CNRS, 118 route de Narbonne, F-31062 Toulouse Cedex, France

³Service National des Champs Magnétiques Pulsés, UMS 5642, F-31077 Toulouse Cedex, France

⁴Laboratoire de Magnétisme et Optique, CNRS-Université de Versailles, 78035 Versailles Cedex, France

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The effects of pulsed magnetic fields and pressure on the spin crossover phenomenon between high-spin and low-spin electronic states in ferrous compounds are investigated by introducing a model based on a macroscopic master equation written in the mean-field approximation. A bidirectional transition is predicted on the spontaneous thermal hysteresis and the light-induced thermal hysteresis (LITH) loops. The model also witnesses that a pressure pulse displays a mirror effect compared to a pulse of magnetic field and that different behaviors can be obtained depending on the intensity and shape of these pulses. In particular, we found that a rather long (~ 1 s) external perturbation must be used to reach a maximal spin conversion. In addition, the pulse intensity necessary to trigger a transition on the LITH loop is at least 30 times higher than for a spontaneous thermal hysteresis loop. As a final theoretical point, the correlation between the cooperativity and the response to a pulsed excitation is presented.

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I. INTRODUCTION

In some transition metal complexes, an electronic transition from a low-spin (LS) to a high-spin (HS) state can be triggered under external perturbations such as temperature,¹ pressure,^{2,3} light irradiation,⁴⁻⁷ or magnetic fields.⁸ The possibility to induce a spin crossover (SCO) by a magnetic field was first demonstrated by Sasaki and Kambara,⁹ who proposed a model based on the ligand field theory, predicting the effect of large static magnetic fields (20–100 T) in ferrous and ferric compounds.⁹ Shortly after, Qi *et al.*¹⁰ experimentally quantified the effect for a lower static field (5.5 T) on the iron(II) SCO compound Fe(phen)₂(NCS)₂. The influence of static magnetic fields of up to 23 T on the SCO phenomenon was also studied later, experimentally as well as theoretically.¹¹ In the future prospects of designing molecular switching devices based on SCO compounds, the use of pulsed magnetic fields for the investigation of the switching dynamics represents an appealing perspective. Until now, experiments on SCO complexes consisted of applying 32 T pulsed magnetic fields of about 1 s.¹² At present, microsecond magnetic fields well beyond this value are available using high-field facilities,¹³ which opens new perspectives for fast triggering of spin transition.

Beside magnetic fields, which can induce a SCO from the LS to the HS state,⁸ recent experimental advances¹⁴ demonstrated that pressure pulses could also be another tool to trigger a spin change from the HS to the LS state. Therefore, pressure has a “mirror effect” compared to magnetic fields. Within this context, using pressure pulses could be a promising way toward the elaboration of writing-erasing sequences at the molecular scale.

In this paper we focus on the effect of magnetic field and pressure pulses on the thermal hysteresis and the light-induced thermal hysteresis (LITH) loops. The present paper is organized as follows: In Sec. II we recall the static and

dynamical versions of the Ising-type model in which we now include different external excitations, such as pressure and magnetic field pulses, and light irradiation. In Sec. III we show and discuss the obtained results using these three perturbations. Section IV is devoted to the study of the cooperativity effect on the response of the system under these various perturbations.

II. THE STATIC AND DYNAMIC ISING-TYPE MODEL

The energy of a system with two energy levels is expressed as a function of the energy gap Δ_0 between the two levels of an isolated molecule and a phenomenological parameter J describing the molecular interactions,¹⁵

$$\hat{H} = \sum_i \frac{\Delta_0}{2} \hat{\sigma}_i - J \sum_{j \neq i} \hat{\sigma}_i \hat{\sigma}_j, \quad (1)$$

where $\hat{\sigma}$ is a fictitious spin operator with eigenvalues of +1 or -1 for the HS and LS states, respectively. Each level in this model represents an effective level including the electronic configuration and the vibrational density of states.

In the mean-field approximation, the analytical solution of the Hamiltonian (1) can be expressed with respect to the HS fraction $\gamma_{HS}(=1 + \langle \sigma \rangle / 2)$ as¹⁶

$$-k_B T \ln \left(\frac{\gamma_{HS}}{1 - \gamma_{HS}} \right) = \Delta_0 - 2zJ(2\gamma_{HS} - 1) - k_B T \ln r, \quad (2)$$

where z is the coordination number and $r = r_{el} r_{vib}$ takes into account the electronic, r_{el} , and vibrational, r_{vib} , effective degeneracy ratio between HS and LS states. The resolution of such an equation of state leads to the thermally activated hysteresis loop when $zJ > k_B T_{eq} = \Delta_0 / \ln r$. By applying a pulsed magnetic field $B(t)$ or a pressure pulse $P(t)$ on a selected point of the theoretical hysteresis loop, it becomes

possible to follow the evolution of the HS fraction under pulsed excitations. We use the master equation, giving the time evolution of the HS fraction, already established in the mean-field approximation.^{8,16,17}

$$\begin{aligned} \frac{d\gamma_{HS}}{dt} = & -\frac{1}{2\tau_0}\gamma_{HS}\exp(-\beta\varepsilon^+)\exp(-2\beta zJ\gamma_{HS}) \\ & +\frac{1}{2\tau_0}(1-\gamma_{HS})\exp(-\beta\varepsilon^-)\exp(2\beta zJ\gamma_{HS}), \end{aligned} \quad (3)$$

with

$$\varepsilon^\pm = E_a^0 \mp \frac{\Delta_0}{2} \mp zJ \pm \frac{k_B T}{2} \ln r \pm C_{pulse}(t). \quad (4)$$

The frequency $1/\tau_0$ defines the individual spin-flip rate between the two states and E_a^0 the vibronic intramolecular energy barrier. The expression of $C_{pulse}(t)$ is written as

$$C_{pulse}(t) = 4 \frac{[\mu_B B(t)]^2}{k_B T}, \quad (5)$$

when considering the effect of a pulsed magnetic field on an iron(II) SCO complex, or

$$C_{pulse}(t) = -\frac{P(t)\Delta V}{2}, \quad (6)$$

to account for the pressure pulse influence.

In Eq. (5), μ_B is the Bohr magneton, and in Eq. (6), ΔV represents the volume change induced by the spin transition ($\Delta V > 0$). Furthermore, it is now well known in SCO systems that at moderate temperatures, a continuous photoexcitation may generate an instability of the steady state that is the transition from a monostable to a bistable behavior.¹⁷ This leads to the so-called light-induced thermal hysteresis.^{18,19} This light-driven spin conversion comes from the competition between the nonlinear thermally activated relaxation of the HS fraction and the photoexcitation process acting on the LS fraction. In the mean-field approximation, previously defined, the time dependence of the HS fraction γ_{HS} under a pulsed excitation is expressed through the following macroscopic master equation:

$$\frac{d\gamma_{HS}}{dt} = I_0\sigma(1-\gamma_{HS}) - \frac{1}{2\tau_0}\gamma_{HS}\exp(-\beta\varepsilon^+)\exp(-2\beta zJ\gamma_{HS}), \quad (7)$$

where $I_0\sigma$ is the photoconversion rate from the LS to the HS state. I_0 is the intensity of the exciting radiation, and σ depends on the light-absorption cross section and the number of absorbing atoms.²⁰ Here, ε^+ is given by Eq. (4) again. It is noteworthy that at low temperatures the thermal $LS \rightarrow HS$ relaxation is hindered by the large energy barrier ε^- in such a way that this process is neglected in Eq. (7). The steady states of Fig. 1 are obtained for $d\gamma_{HS}/dt=0$.²¹

To visualize the stability properties of the steady states under permanent irradiation, we use the concept of the dynamical potential.^{16,17,22} We express the flux $d\gamma_{HS}/dt$ as a force deriving from the dynamical potential U , which gives

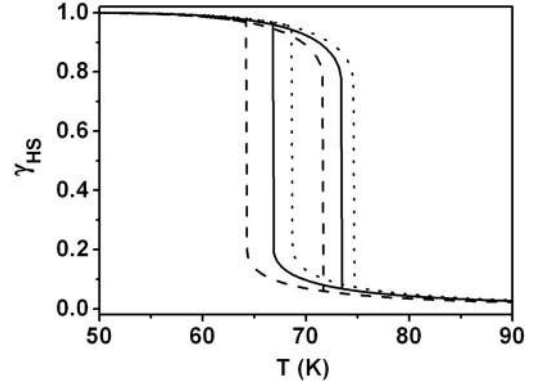


FIG. 1. Effect of static pressure and static magnetic field on the light-induced thermal hysteresis loop in the absence of external perturbations (straight line), in a static magnetic field of 20 T (dotted line), and under a hydrostatic pressure of 200 bar (dashed line). Parameter values are $E_a^0=1000$ K, $\Delta_0=1000$ K, $zJ=200$ K, $r=200$, and $I_0\sigma\tau_0=3 \times 10^{-5}$.

$$\frac{d\gamma_{HS}}{dt} = -\frac{\partial U}{\partial \gamma_{HS}}. \quad (8)$$

By inserting the expression (3) or (7) of the flux and integrating Eq. (8), the dynamic potential without or under continuous irradiation can be written, respectively, as^{16,17}

$$\begin{aligned} U(\gamma_{HS}, T) &= -\frac{1}{2\tau_0} \left[\frac{\exp(-\beta\varepsilon^+)}{2\beta zJ} \exp(-2\beta zJ\gamma_{HS}) \left(\frac{1}{2\beta zJ} + \gamma_{HS} \right) \right. \\ &\quad \left. + \frac{\exp(-\beta\varepsilon^-)}{2\beta zJ} \exp(2\beta zJ\gamma_{HS}) \left(1 + \frac{1}{2\beta zJ} - \gamma_{HS} \right) \right], \end{aligned} \quad (9)$$

or

$$\begin{aligned} U(\gamma_{HS}, T) = & I_0\sigma \left(\gamma_{HS} - \frac{\gamma_{HS}^2}{2} \right) - \frac{1}{2\tau_0} \left[\frac{\exp(-\beta\varepsilon^+)}{2\beta zJ} \right. \\ & \left. \times \exp(-2\beta zJ\gamma_{HS}) \left(\frac{1}{2\beta zJ} + \gamma_{HS} \right) \right], \end{aligned} \quad (10)$$

which leads to the double-well potential characterizing the bistable situation of SCO complexes^{16,17} undergoing static perturbations (Fig. 2). A static magnetic field stabilizes the HS state at the expense of the LS state²³ due to the Zeeman effect, whereas a hydrostatic pressure induces the opposite effect because the LS molecules are less voluminous than HS ones.²⁴ The LITH loop (spontaneous thermal hysteresis loop) is shifted upward (downward) or downward (upward) under static magnetic fields or pressures, respectively (Fig. 1). In fact, in the case of a continuous irradiation at low temperature, the potential energy of the HS state is not really affected by external excitations, whereas that of the LS state is drastically modified [(Fig. 2(b))].

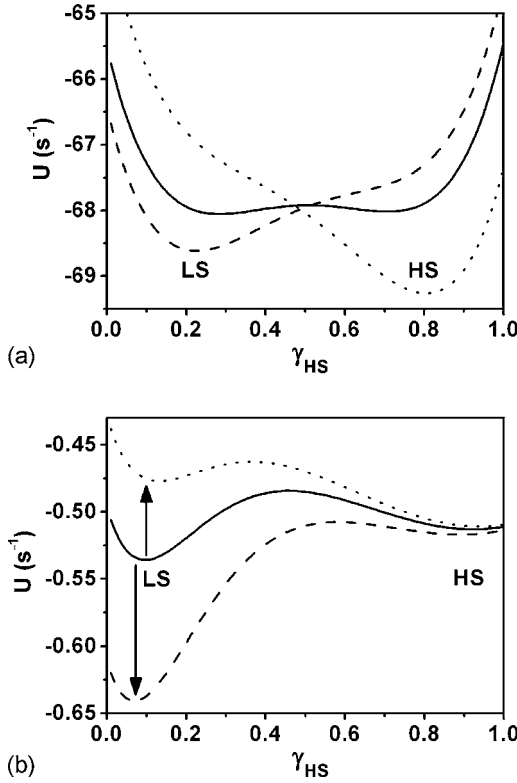


FIG. 2. (a) Dynamical potential associated with the bistable situation of the $\text{Fe}(\text{phen})_2(\text{NCS})_2$ in the absence of external perturbations (straight line), in a static magnetic field of 32 T (dotted line), and under a hydrostatic pressure of 80 bar (dashed line). Parameter values are $E_a^0=173$ K, $\Delta_0=1034$ K, $zJ=188$ K, $r=354$, $\tau_0=2.5 \times 10^{-3}$ s, and $T=T_c \approx 176.1$ K. (b) Dynamical potential for parameter values of Fig. 1 at $T=70$ K in the absence of external perturbations (straight line), in a static magnetic field of 20 T (dotted line), and under a hydrostatic pressure of 200 bar (dashed line).

III. EFFECT OF MAGNETIC FIELD AND PRESSURE PULSES ON THE SPIN CROSSOVER PHENOMENON

The influence of pulsed magnetic fields and pressures on the thermal hysteresis loop is investigated through the study of the well-documented SCO complex $\text{Fe}(\text{phen})_2(\text{NCS})_2$,^{25–28} whose electronic degeneracy ratio r_{el} is known to be equal to five, whereas the energy gap Δ_0 and the vibrational degeneracy ratio r_{vib} can be evaluated from calorimetric measurements,²⁵

$$\begin{cases} \Delta_0 = 1034 \text{ K} \\ r_{vib} = \frac{1}{r_{el}} \exp\left(\frac{\Delta S}{R}\right) \approx 70.8 \end{cases}$$

The value of zJ , namely, $zJ=188$ K, is extracted from former theoretical studies, in the mean-field approximation, about the application of static magnetic fields on the SCO compound $\text{Fe}(\text{phen})_2(\text{NCS})_2$.²⁶ For this parameter value, the critical temperature T_c ($T_c \approx 176.1$ K) and the width of the thermal hysteresis loop ΔT ($\Delta T \approx 1.3$ K) are very close to experimental data,²³ even if mean-field methods are known to overestimate hysteresis widths. However, at 165 K (190 K) the calculated HS fraction is around 0.1 (0.9), al-

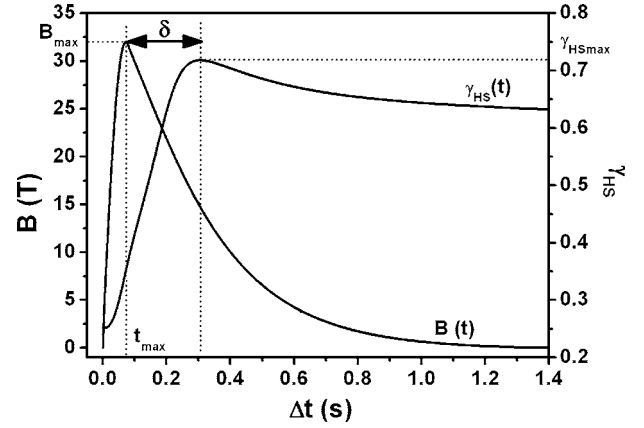


FIG. 3. Time dependence of the experimental magnetic field pulse available in the SNCMP and of the HS fraction induced by this field. The delay δ between the maximum of the magnetic field B_{max} and the maximal HS fraction γ_{HSmax} reached by the excited SCO compound is also defined.

though experimentally the system is in the pure LS (HS) state below 170 K (above 190 K). The activation energy E_a^0 is equal to 173 K,²⁹ the volume change ΔV is 18 \AA^3 per molecule,³⁰ and the intrinsic frequency $1/\tau_0$ is evaluated to be 400 s^{-1} by comparing the steepness of theoretical and experimental magneto-induced jumps of HS fraction after a pulsed magnetic field excitation.²³ This latter value is in fairly good agreement with previous findings¹⁶ in the mean-field approach.

A. Effect of a pulsed magnetic field in the region of the spontaneous thermal hysteresis loop

Experimental pulsed magnetic fields are produced by a discharge of a capacitor bank (1.25 MJ, 25 000 μF) into a resistive copper coil.¹² They typically consist of a quarter of a sine increase during 75 ms and up to 32 T followed by an exponential decay (Fig. 3). The whole time duration of the pulsed excitation is then defined as the time separation between the application of the magnetic field and the instant when it falls down to 0.01 T after reaching its maximum.

So as to compare experimental and theoretical results, an experimental-like magnetic pulse is inserted in the master equation (3), which leads to the results plotted in Figs. 4(b) and 4(c), which are qualitatively in good agreement with the observed experimental data^{12,23} [Figs. 4(e) and 4(f)]. On the ascending branch, the magnetic field destabilizes the metastable LS state and triggers an irreversible transition. On the descending branch, the magnetic field stabilizes an already stable HS state, and the effect is reversible. In other words, a pulsed magnetic field favors a $LS \rightarrow HS$ spin conversion, as predicted by the behavior of the dynamical potential under a static magnetic field [Fig. 2(a)].

However, on the ascending branch, experimental jumps are nearly two or three times weaker than theoretical ones. (Hops $\Delta\gamma_{HS}$ satisfy the relation $\Delta\gamma_{HS} = \gamma_{HS}^{final} - \gamma_{HS}^{initial}$.) This stems from the fact that the mean-field approximation involves a homogeneous repartition of the two molecular states in the crystal whereas a phase separation occurs during the

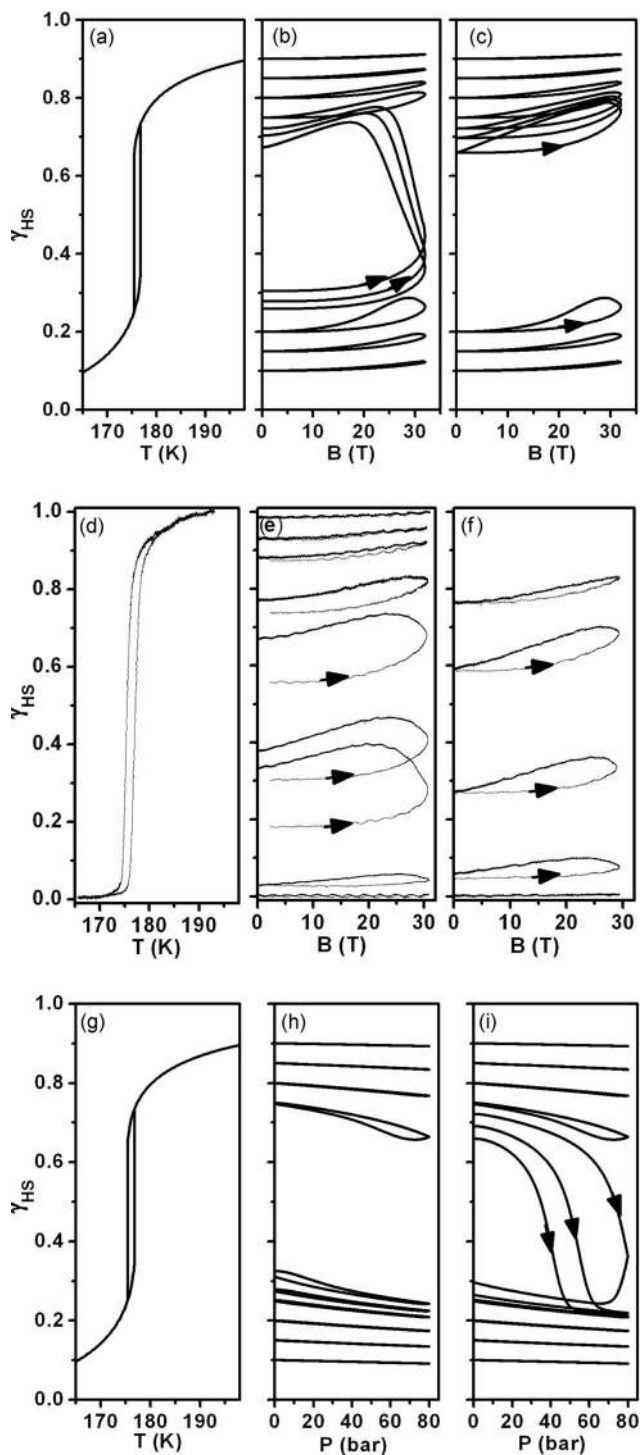


FIG. 4. Calculated [(a) and (g)] and experimental (d) thermal hysteresis loop of $\text{Fe}(\text{phen})_2(\text{NCS})_2$. Simulation of the effect of a 32 T pulsed magnetic field applied on the ascending (b) and descending (c) branches of this thermal hysteresis loop. Complete set of pulsed field experiments in the ascending (e) and descending (f) branches of the thermal hysteresis loop of $\text{Fe}(\text{phen})_2(\text{NCS})_2$. Arrows indicate the direction of the spin transition ($LS \rightarrow HS$ here). Theoretical effect of applying a 80 bar triangular pressure pulse (1.4 s with its maximum at $t_{max}=0.7$ s) on the ascending (h) and descending (i) branches of this thermal hysteresis loop. Arrows indicate the direction of the spin transition ($HS \rightarrow LS$ here).

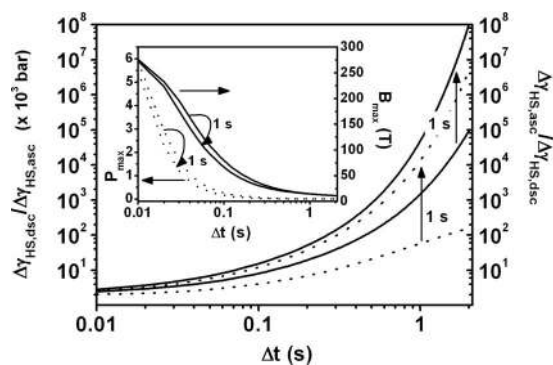


FIG. 5. Evolution of the ratio of hops on the ascending ($\gamma_{HS}^{initial} \approx 0.34$) and on the descending ($\gamma_{HS}^{initial} \approx 0.66$) branches as a function of its duration in the case of the experimental pulsed magnetic field (straight line and right-hand side) and the triangular pressure pulse also used in Fig. 4 (dotted line and left-hand side). For each duration, the excitation magnitude is optimized to obtain the maximal ratio. Maximal values of these pulsed excitations are plotted on the inset. Each set of two curves corresponds to data collected immediately after the pulse application and after a 1 s relaxation.

spin crossover. A genuine quantitative approach would imply the consideration of the phase demixion process at the origin of thermally induced formation and growth of spin domains,^{31–35} whose dynamics would be rather difficult to reproduce theoretically. As a consequence, the ratio of jumps on the two branches $\Delta\gamma_{HS,asc}/\Delta\gamma_{HS,dsc}$ appears to be a better physical observable than $\Delta\gamma_{HS}$ in the mean-field approximation, since in the ideal case of a pure reversibility on the descending branch, such a ratio should be infinite and does not depend a lot on the numerator.

Figure 5 displays the maximal ratio $\Delta\gamma_{HS,asc}/\Delta\gamma_{HS,dsc}$ with respect to the pulse duration Δt and the optimized intensity B_{max} . For short pulses ($\Delta t < 100$ ms), the decrease in time cannot be totally compensated by an increase in field intensity, even by optimizing this field. Furthermore, the states reached after an intense magnetic excitation are sometimes unstable and the expected stable state is obtained only after a few seconds of relaxation ($B=0$). After a 1 s relaxation, indeed, this stable state is attained for most initial HS fractions both on the ascending and on the descending branches for sufficient pulse durations (approximately 1 s). Within the same context, the replacement of the experimental-like pulsed excitation by a triangular-shape pulsed magnetic field leads to the production of weaker (100 times weaker for pulse durations of 2 s, that is, 1 s for the increase in magnetic field and 1 s for the decrease) jumps, despite the maintenance of a neat irreversibility on the ascending branch and reversibility on the descending one after a 1 s relaxation. Therefore, triggering a SCO in some milliseconds seems to be excluded by exciting the bulk material, since it requires at least a 100 ms excitation and even a 1 s relaxation sometimes. A detailed study of the relaxation process based on the master equation (3) was previously realized by one of the authors,¹⁶ both outside and within the hysteresis loop for SCO compounds, and is beyond the scope of this paper.

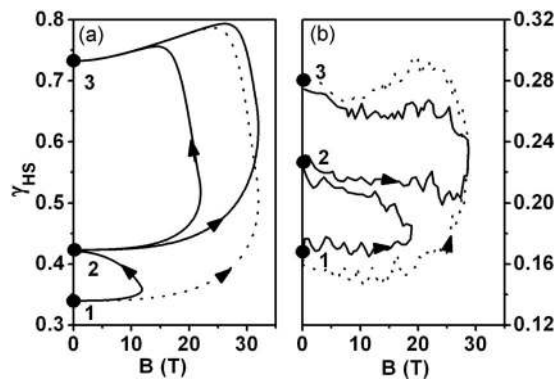


FIG. 6. (a) Theoretical effect of applying successively two magnetic field pulses on the SCO complex $\text{Fe}(\text{phen})_2(\text{NCS})_2$ at 176.7 K. The effect of a 12 T+22 T and a 12 T+32 T sequence of pulses (straight lines), and that of a single 32 T pulsed magnetic field (dotted line), are presented. (b) Experimental evidence of the effect of successively applying two magnetic field pulses of 20 T and 29 T (straight lines) and a single 29 T magnetic pulse on the ascending branch of the SCO complex $[\text{Fe}_x\text{Ni}_{1-x}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ with $x=0.52$ at around 134 K. Arrows indicate the direction of the spin transition ($LS \rightarrow HS$ here).

One can add that after applying a magnetic perturbation, any unstable excited state can generate the buildup of two stable states as shown above [Fig. 2(a)], the potential well associated to the initial HS fraction on the hysteresis loop and another to a mainly HS final state. To each initial HS fraction corresponds a magnetic field threshold below which spin transition cannot occur. Its value is 12 T for $\gamma_{HS}^{initial} \approx 0.34$ and increases to 28 T for $\gamma_{HS}^{initial} \approx 0.26$, which explains the irreversible transition due to the application of a 32 T pulsed magnetic field [Fig. 4(b)]. This bistability also involves that several successive pulses cannot lead to the pure HS state, whatever their intensities. For example, for $\gamma_{HS}^{initial} \approx 0.34$, the application of a 12 T followed by a 22 T pulsed magnetic field yields a final state which cannot be modified by applying even more intense (32 T for instance) additional magnetic pulses. Moreover, a 12 T+32 T sequence leads to the same final state as a single 32 T pulsed magnetic field, which is experimentally observed too (Fig. 6). Both the 12 T+22 T and 12 T+32 T sequences and a 32 T pulse trigger a spin crossover to the metastable HS state associated with the chosen initial condition thereby.

In the perspective of switching devices using SCO materials, the acceleration of the information writing process requires abrupt commutation from one state to the other, that is, to reduce the switching time directly linked to the delay δ , between the maximum of the magnetic exciting field B_{max} and that of the response of the medium γ_{HSmax} (Fig. 3). Such delays have been experimentally determined by Bousseksou *et al.*,^{12,23} who notably showed they were close to 100 ms (25 ms) on the ascending (descending) branch for an initial HS fraction $\gamma_{HS}^{initial}$ close to 0.3 (0.7) in the case of $\text{Fe}(\text{phen})_2(\text{NCS})_2$. These values are compatible with delays of 122 ms (27 ms) calculated in the mean-field approach with the same initial conditions.

It also turns out that the delay decreases when the maximum of the magnetic pulse B_{max} [Fig. 7(a)] rises, on the

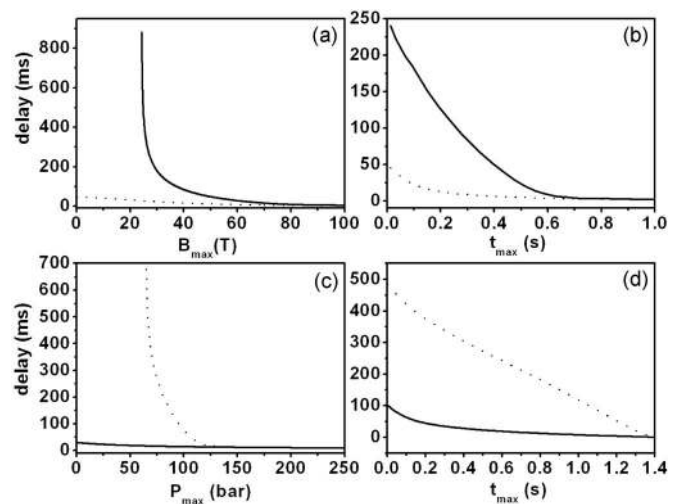


FIG. 7. Effect of the intensity (a) and the shape (b) of a pulsed magnetic field [(c) and (d), respectively for a pulsed pressure] on the delay between the magnetic excitation and the response on the ascending (straight line for $\gamma_{HS}^{initial} \approx 0.28$) and descending (dotted line for $\gamma_{HS}^{initial} \approx 0.73$) branches of thermal hysteresis loops. t_{max} denotes the moment when the maximal pulse intensity is reached.

ascending and on the descending branches as well. On this latter branch, the response time is not affected significantly yet because the induced relative stability of the HS state prevents any irreversible transition. On the ascending branch, the shortest delays result from magnetic pulses energetic enough to induce a maximal spin conversion by jumping over the activation energy barrier, and they are accordingly related to the steepest hops $\Delta\gamma_{HS}$ obtained for $B_{max} > 40$ T (for $\gamma_{HS}^{initial} \approx 0.28$). On the contrary, for $B_{max} < 24$ T, the irreversibility becomes much less marked and even tends to disappear completely on the ascending branch due to the insufficient pulse energy.

The delay is also sensitive to the pulse shape [Fig. 7(b)]. An investigation of the influence of this parameter can be brought about by changing the value of t_{max} , instantly associated to the maximum B_{max} of the experimental magnetic pulse (Fig. 3) and whose enhancement automatically induces a longer quasilinear slope and a faster exponential decay. In particular, for $t_{max} > 0.6$ s, the delay is minimized, namely, lower than 10 ms, and the speed of the response is accordingly maximized. An instantaneous spin crossover can only be expected for intense pulsed magnetic fields which reach rather slowly their maximal value hence. Nevertheless, bistable nanoparticles, which cannot be studied in the framework of the present macroscopic approach, might convert much more quickly under the effect of a magnetic pulse. Indeed, in such a case, a rapid nucleation is expected at the surface, in which large fluctuations of the spin states are enhanced by the reduced number of surrounding neighbors. In addition, the threshold value of the magnetic field required for the switching will be drastically reduced in small nanoparticles. As a consequence, a total and rapid switching between the LS and HS states becomes possible using small fields. The theoretical part of this specific problem will be addressed using Monte Carlo simulations (now in progress) in a separate contribution.

B. Effect of a pulsed pressure in the region of the spontaneous thermal hysteresis loop

As formerly pointed out,^{8,10,12} the influence of the application of a (static or pulsed) magnetic field can be interpreted as a negative temperature shift of the hysteresis loop. The temperature shift caused by 1 T is then roughly opposite to the effect of 2.5 bar. Consequently, a pressure pulse of only 80 bar should lead to the same jumps in magnitude as the magnetic pulse of 32 T, except that the irreversibility occurs on the descending branch and the reversibility on the ascending one; pressure has a “mirror effect” compared to the application of an intense and pulsed magnetic field.¹⁴

From now on, the theoretical 1.4 s pulsed pressure excitation will correspond to a 700 ms linear increase up to 80 bar followed by a 700 ms linear decay. By employing such a pressure pulse, our calculations reveal that the system undergoes a purely reversible evolution on the ascending branch of the thermal hysteresis loop [Fig. 4(h)], while a jump in the HS fraction may occur on the descending branch [Fig. 4(i)]. In fact, in this latter case, first the system reaches a transient state and the final stable state is recovered after some relaxation time (Fig. 5). One can add that this final state cannot be the pure LS one, as suggested by the position of minima in the double-well potential under static pressures [Fig. 2(a)]. Besides, even experimentally, only a partial switching ($|\Delta\gamma_{HS}|=35\%$) can be triggered by applying a pressure pulse of 110 bar from an initial HS fraction of 0.75.¹⁴

The intensity and the speed of the response of the material to a pulsed pressure excitation is governed by the characteristics of this perturbation as for the application of a pulsed magnetic field. For pressures P_{max} higher than 220 bar and slow increases in pressure, namely, during ~ 1.3 s, the delay between the excitation and the response of the medium does not exceed 10 ms [Figs. 7(c) and 7(d)]. For P_{max} going from 220 to 65 bar, this delay rapidly grows and the conversion efficiency falls hence (although a few seconds of relaxation yields the same final HS fraction as the 220 bar perturbation whatever the value of P_{max} in the 65–220 bar pressure range). Finally, for too weak pressure pulses ($P_{max} < 65$ bar), that is for low excitation energy, HS molecules cannot even be converted to LS ones.

All these observations suggest that a stable form can be produced by reasonably weak pulsed pressure excitations, but this conversion is rather sluggish and switching speeds of a few milliseconds (or less, as it would be preferable for potential applications) seem not achievable.

C. Effect of a pulsed magnetic field and pressure on the LITH loop

The only experimental study on the magnetic field effect on the light-induced spin-state transition between LS and HS states was carried out by Ogawa *et al.*,³⁶ who showed that at 10 K, a static magnetic field stabilizes the photoconverted HS state of the SCO complex $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ (2-pic = 2-amino-methyl-pyridine) compared to the LS state. In contrast, from a theoretical point of view, recent studies going beyond the mean-field approach and combining magnetic

and SCO phenomena under light have attracted much more interest.^{37,38} Here, we focus on the pulsed magnetic field or pressure influence on photoinduced states.

Unlike the thermal hysteresis loop, a 32 T pulsed magnetic field or a 80 bar pressure pulse of 1.4 s applied on whatever branch of the LITH loop do not trigger a neat spin transition. The physical reason for this failure is due to the difference in time scale of the relaxation process from the HS state at high and low temperatures. Indeed, it is worth noting that the effect of a pulsed magnetic field is essentially a kinetic effect. It is well known that at high temperature (170–200 K), *i.e.*, around the spontaneous thermal hysteresis, the typical relaxation times are of the order of magnitude of a few milliseconds.³⁹ In contrast, at low temperatures (20–60 K, in the LITH region) the relaxation time of the photoinduced HS fraction is of the order of magnitude of a few hours. Knowing that the transition probability per unit time is directly related to these lifetimes,¹⁶ it becomes clear that it is more difficult (at least a thousand times) to trigger the HS phase by a magnetic pulse at low temperature than at high temperature.

Indeed, our simulations show that to trigger the $LS \rightarrow HS$ transition by pulsed magnetic field on the LITH branches, the maximum P_{max} of the pulsed pressure and B_{max} of the pulsed magnetic field must be respectively higher than 2.5 kbar and the unrealistic value of 6500 T if considering a 1.4 s pulse duration. Such a 2.5 kbar pulsed pressure does not affect the SCO system if applied on the ascending branch, whereas it may trigger a 83% spin conversion on the descending one at $T=70$ K for parameter values listed in Fig. 1. Nevertheless, it is worth noticing that even if multiplying their duration by 1000, a 32 T pulsed magnetic field or a 80 bar pulsed pressure cannot induce any transition.

IV. EFFECT OF THE COOPERATIVITY ON THE RESPONSE TO A PULSED EXCITATION

Metal-diluted mixed crystals are relevant systems to study the role of elastic interactions, also called cooperative interactions, in the SCO phenomenon.^{40–42} In these materials, the dilution ratio and the size of the molecules which do not undergo a SCO impose the magnitude of these interactions. Qualitatively, the spin change of a SCO metal center from the LS to the HS state generates a rise in the molecular volume, leading to an expansion of the lattice. This produces an internal pressure change acting on all complex molecules in the crystal and favors the conversion of other SCO metal centers. The interactions involved in this process are long-range type and hence, well reproduced by mean-field treatments.⁴⁰

Long-range elastic interactions manifest themselves through the abruptness of spin crossover and the width of spontaneous and light-induced thermal hysteresis.²¹ The inset in Fig. 8 shows the measurements of experimental delays between the excitation and the response of SCO systems by investigating the effect of a 32 T pulsed magnetic field on the family of diluted complexes $[\text{Fe}_x\text{Ni}_{1-x}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$,⁴³ for which the dilution parameter x controls the cooperativity. The largest x values are then

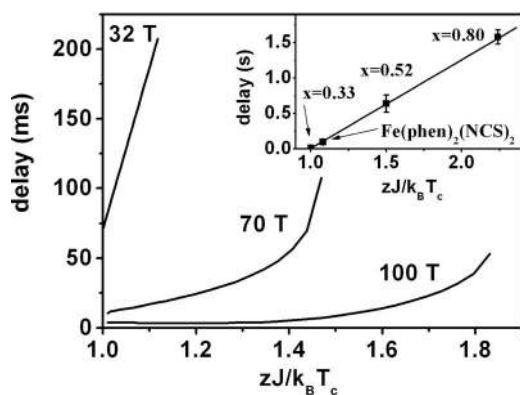


FIG. 8. Theoretical time separation (delay) between $B^{\max}(t)$ and $\gamma_{HS}^{\max}(t)$ on the ascending branch with respect to $zJ/k_B T_c$ for pulsed magnetic fields of 100 T, 70 T, and 32 T. Parameter values are $E_a^0 = 173$ K, $\Delta_0 = 1034$ K, $r = 354$, $\tau_0 = 2.5 \times 10^{-3}$ s, and $T = T_c$. The inset shows the influence of a 32 T pulsed magnetic field on the same time separation (for initial temperatures corresponding to a molecular fraction $\gamma_{HS}^{\text{initial}} = 0.4$ on the ascending branch) as a function of $zJ/k_B T_c$ for the $[\text{Fe}_x \text{Ni}_{1-x}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ with $x = 0.33$, 0.52, and 0.80, and for $\text{Fe}(\text{phen})_2(\text{NCS})_2$.

associated to the strongest elastic interactions, that is, the most important $zJ/k_B T_c$ ratios. In fact, the response time of a SCO system to an external perturbation is related to the zJ variation, because it is imposed by the relaxation time from the HS to the LS state that is by the energy barriers between the two states which depend on the zJ parameter.

More accurately, the experimental delay follows a linear law with respect to the cooperativity, which is exactly reproduced in our mean-field approach for a 32 T pulsed excitation (Fig. 8). In contrast, for higher fields the dependence is not linear. This perfectly matches the above-mentioned decrease in delay parallel to the magnetic field enhancement [Fig. 7(a)]. At 100 T, for example (Fig. 8), the response time does not depend on elastic interactions as much as at 32 T or 70 T. It is somewhat constant. The jump in HS fraction sharply varies as a function of the zJ parameter. A 100 T pulsed magnetic field effectively ensures a quasitotal conversion ($|\Delta \gamma_{HS}| > 80\%$) from the LS to the HS state for $zJ > 240$ K, namely, $zJ/k_B T_c > 1.4$. Below this value the switching is much less efficient and drops, decreasing the cooperativity. This is in good agreement with former experi-

mental and theoretical findings about $\text{Co}[\text{H}_2(\text{fsa})_2\text{en}](\text{py})_2$ and $\text{Fe}(\text{phen})_2(\text{NCS})_2$ complexes.⁸ This latter compound leads to jumps 60% weaker than the more cooperative $\text{Co}[\text{H}_2(\text{fsa})_2\text{en}](\text{py})_2$ complex.

By considering the above-mentioned mirror effect of the pressure compared to the magnetic field, the same tendencies are obtained with respect to the cooperativity. For a 80 bar pulsed perturbation applied on the descending branch of a thermal hysteresis loop, the delay linearly rises from $zJ/k_B T_c > 1.05$ ($zJ > 185$ K), whereas at 1 kbar it is nearly equal to 3 ms up to $zJ/k_B T_c = 1.9$ ($zJ = 320$ K), and a spin conversion higher than 80% systematically happens for $zJ/k_B T_c > 1.7$ ($zJ > 290$ K). Both pressure and magnetic perturbations induce a significant phase transition from the LS to the HS and from the HS to the LS state, respectively, for strongly cooperative compounds thereby.

V. CONCLUSION

We have reported here a theoretical approach based on the dynamical mean-field approximation to study the effect of pulsed perturbations (magnetic field or pressure) on SCO compounds. The analysis was carried out in the spontaneous thermal hysteresis loop or in the LITH hysteresis loop regions. This approach describes successfully various behaviors, such as the mirror effect between magnetic field and pressure or the influence of the cooperativity parameter on the response of the system to a pulsed excitation. A magnetic field induces an irreversible transition on the ascending branch and a pressure pulse on the descending one. The low pressures needed to observe such a spin change seem particularly promising.

We have identified that pulse modeling may induce faster dynamics. In particular, the pulse duration, its intensity, and shape are important factors involving deep changes in the response of the molecular system at the macroscopic level. In the framework of the present mean-field model, it seems, however, that switching times around milliseconds or less are not feasible when addressing the system with a magnetic field or a pressure pulse.

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*Corresponding author. Email address: kbo@physique.uvsq.fr

†Corresponding author. Email address: boussek@lcc-toulouse.fr

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