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Dynamic triggering of a spin-transition by a pulsed magnetic field*

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Abstract. We report the first study of the effect of a high pulsed magnetic field on a spin transition complex in the solid state. The high spin fraction was determined by optical reflectivity. Sizeable effects are observed for the well-known spin transition solid $\mathrm{Fe(Phen)_2(NCS)_2}$. In the hysteresis loop temperature range, an increase in the HS fraction is obtained, with an irreversible (reversible) character in the ascending (descending) branch of the loop. The time dependence of the HS fraction provides information on the kinetics of the spin-crossover process at the spin transition.

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1 Introduction

In some transition metal complexes, a change of electronic state (spin-crossover) from a low spin (LS) to a high spin (HS) state can be induced by changing the temperature or the pressure, or by light irradiation [1]. Due to the role of intermolecular interactions, the crossover may occur abruptly, as a function of temperature, leading to a first-order transition, usually exhibiting hysteresis. Typical examples are provided by $\mathrm{Fe^{II}}$ surrounded by 6 N atoms, such as in the well-known complex $\mathrm{Fe(Phen)_2(NCS)_2}$ [2–5] under study here.

The LS ↔ HS switching is usually detected by Mössbauer spectroscopy (the LS and HS states show different quadrupole interactions), magnetic susceptibility (for $\mathrm{Fe^{II}}$, the spin states are 0, 2) or by optical absorption or reflectivity (the optical properties are different in the LS and HS states) [1].

The application of a static magnetic field stabilises the HS form, with a downwards shift of the transition temperature which is a quadratic function of the intensity of the applied field [4,6]. The effect is small and intense magnetic fields are needed. For example, a 5.5 T static field, applied to the complex studied here, shifted the transition temperature by only ~ -0.12 K [4], while a 22 T static field shifted the equilibrium temperature of a $\mathrm{Co^{III}}$ complex by ~ -0.6 K [6]. Therefore it is of interest to use pulsed magnetic fields, which may reach high values, ~ 50 T and higher. However the main obstacle with pulsed fields was the detection of the spin fractions, which can no longer be obtained by the usual magnetic methods. The experiment has been made possible by the use of optical reflectivity detection, as in [6] (see also [7,8] for recent developments of this method).

2 Sample

$\mathrm{Fe(Phen)_2NCS_2}$ is a well-documented spin-crossover complex [2–5]. The extracted form was synthesised as described in [5]. Variable temperature magnetic susceptibility data, in low applied fields, show an abrupt spin-crossover around $T_\mathrm{c} = 176$ K.

3 Experimental set-up

The fraction of molecules in the high spin state n_HS is determined by reflectivity measurements, using a 5 mW He-Ne laser with $\lambda = 632.8$ nm.

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* Dedicated to Professor René Poilblanc on the occasion of his retirement.

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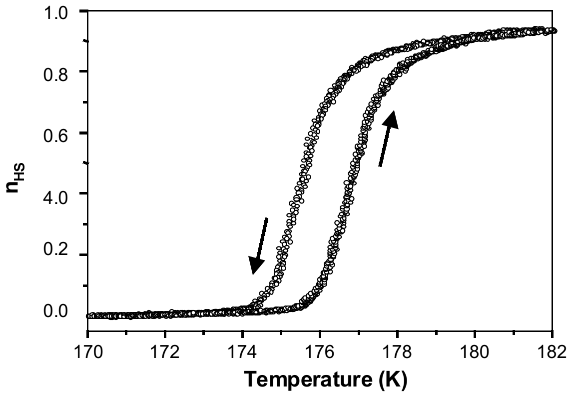

Fig. 1. Fe(phen)$_2$(NCS)$_2$, the thermal hysteresis of the spin transition, in zero applied field, detected by optical reflectivity. The total sweep time is 80′.

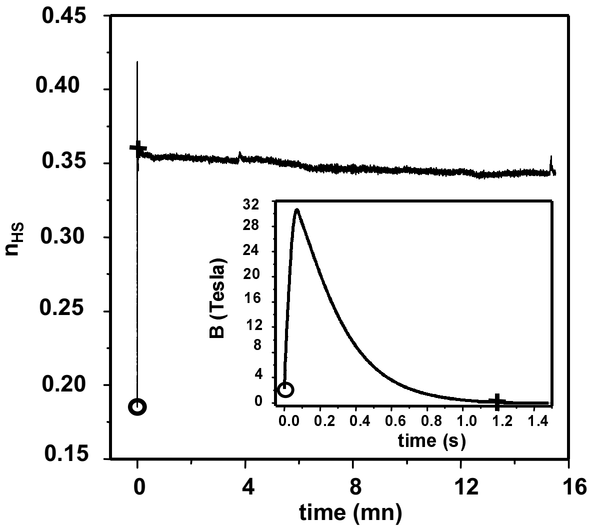

Fig. 2. Fe(phen)$_2$(NCS)$_2$, a typical pulsed field experiment, showing the irreversible jump in the HS fraction (top curve). In the insert is shown the time dependence of magnetic field pulse. The initial state is shown by an open circle.

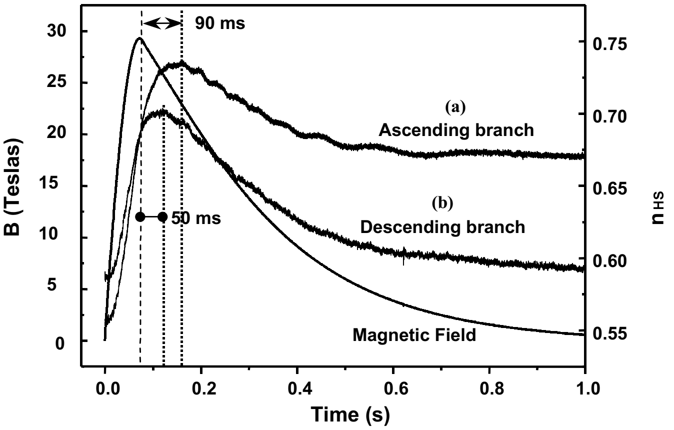

Fig. 3. Fe(phen)$_2$(NCS)$_2$, the time dependencies of two typical responses, for initial states belonging to the ascending (a) and descending (b) branches of the thermal hysteresis loop. For comparison, the time dependence of the magnetic field pulse is also shown.

The radiation reaches the sample through one branch of a split stack of optical fibers. The reflected intensity (I_r) is measured at the output of the other branch by a Si PIN photodiode.

In order to account for the effects of laser intensity fluctuations, a fraction of the incident light intensity (I_0) is simultaneously recorded with the same type of detector. According to previous studies [8], the ratio I_r/I_0 varies $\sim$ linearly as a function of n_{HS}. This ratio was recorded either *versus* temperature or magnetic field.

Magnetic fields up to 32 T were provided by the pulsed field facility of the SNCMP (authors N.N. and M.G.) and Laboratoire de Physique de la Matière Condensée (INSA, Toulouse, France). The quasi-static pulsed field is obtained by the discharge of a capacitor bank (1.25 MJ, 25 000 μF) into a resistive copper coil. The wave form of the increasing field is a quarter of a sine wave and the maximum field is reached in 75 ms, the magnetic field then decreases to 0 in 1.3 s following an exponential law due to the use of a "crowbar" system [9].

The magnetic field was applied at different temperatures. For each measurement in the ascending (descending) branch of the hysteresis loop, the sample was initially reset at 150 K (200 K) before setting the desired temperature value. 10 minutes were allowed for the sample and holder to reach complete thermal stability, and then the magnetic field was applied.

The sample was a pure microcrystalline powder, of $\sim$ 15 mg, enclosed in a cylindrical holder made of insulating matter. The temperature was stabilised by using a self-control system (Lakeshore 330).

4 Results

4.1 Optical reflectivity detection

The optical detection and the temperature control were first checked in absence of an external field. The thermal variation of the high spin fraction $n_{HS}(T)$ obtained by reflectivity in the cooling and heating mode is shown in Figure 1. Using a low sweep rate (5 mK/s) a hysteresis of 1.3 K is obtained. This result agrees very well with the previous data obtained by magnetic susceptibility [3,5].

4.2 High-field measurements

We have observed the largest variations in the intensity of the optical signal, displayed in Figures 2–4, for initial temperatures belonging to the hysteresis range, *i.e.* at the steepest part of the conversion curve (as confirmed by other samples).

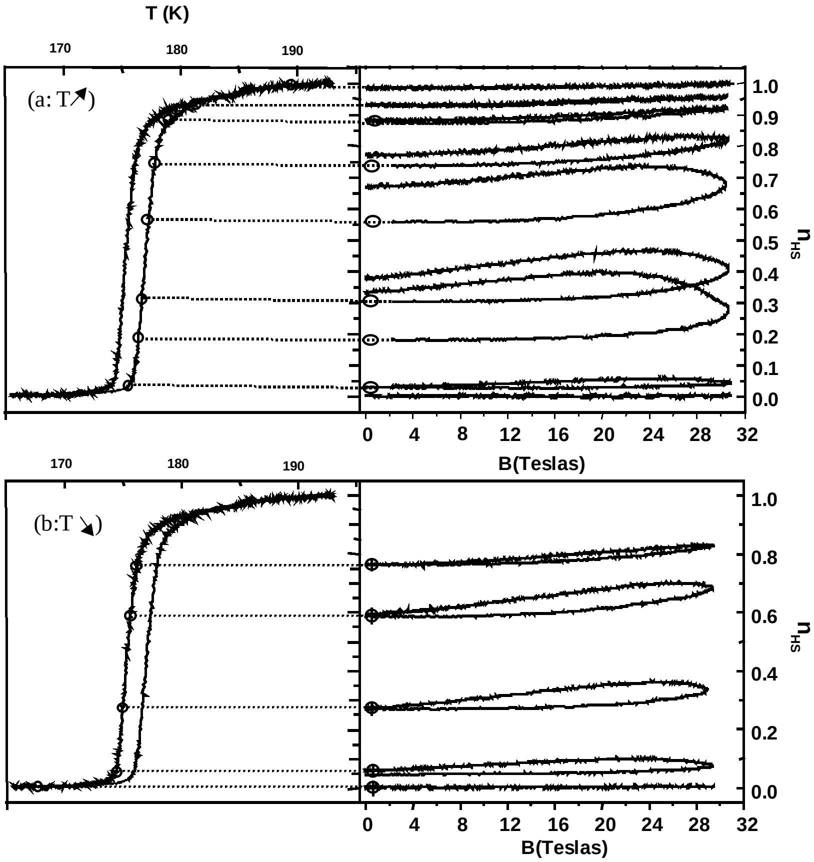

Fig. 4. Fe(phen)$_2$(NCS)$_2$, the complete set of pulsed field experiments in the ascending (a) and descending (b) branches of the thermal hysteresis loop. Initial states are shown by open circles.

In Figure 2 we show a typical field-induced irreversible jump in the optical signal, evidencing for a sizeable triggering of the phase transition. The magnetic field pulse was applied for an initial state of the sample belonging to the ascending branch of the hysteresis loop (warming mode), at $T = 176.1$ K. The irreversible character of the field-induced effect is evidenced by the observation over a rather long time (15 minutes), which shows the stability of the optical signal intensity once the jump has taken place.

Several experiments for various initial states along the ascending and descending branches of the thermal hysteresis loop showed systematic differences in the corresponding field-induced effects. The data are plotted in Figures 3, 4, and reported as follows.

In Figure 3, we have selected two typical time dependencies of the optical response to the applied magnetic field, revealing the transient regimes during and immediately after the pulse. The response curves are compared to the time dependence of the field, (excitation of the system), and exhibit sizeable delays between the maximum field value and the maximum optical response value. The existence of such delays between excitation and response evidences the kinetic character of the process. In other words, the kinetics of the field-induced transformation is not fast with respect to the pulse risetime, ~ 75 ms.

More precisely, in Figure 3, we had selected two experiments performed with ~ the same initial HS population, but starting from either branch of the thermal hysteresis loop. For the ascending (resp. descending) branch, the long time field-induced effect was irreversible (resp. reversible), and the delay for the maximum values markedly differed: 90 and 50 ms, respectively.

The complete set of data is better displayed using response (n_{HS}) *vs.* excitation (B) plots (Figs. 4a, 4b). The phase shift between the signals gives the curve an hysteretic aspect. According to its reversible or irreversible character, the loop appears closed or open, respectively.

The data collected in Figure 4 confirm the close correlation between the presence of an reversibility (resp. irreversibility) in n_{HS} and the choice of the initial state on the descending (resp. ascending) branch of the thermal hysteresis loop. A correlation is also observed between the magnitude of the effect ($\delta n_{\mathrm{HS}}/B_{\mathrm{max}}$) and the slope of the transition curve $\partial n_{\mathrm{HS}}/\partial T$. It also appears from Figure 4 that the delay value depends on the initial HS fraction. For some of the curves, when the loop is narrow, the quadratic dependence of the effect upon the applied field is clearly observed.

Before discussing these data, it is worth emphasizing a crucial experimental aspect. Indeed, owing to the striking difference which appears when the initial states belong to the ascending and descending branches (separated by only 1.3 K!), it is now clear that the preparation of the initial state is of outermost importance. Any temperature fluctuation occurring at the edges of the hysteresis loop will induce an irreversible change; in other words, the definition of the initial state also requires the knowledge of the past thermal history. These effects are well-described in terms of "major" and "minor" hysteresis loops, whose properties are beautifully illustrated by the phenomenological Preisach model [10,11]. Therefore, the following discussion will only focus on the main trends of the data, and will not concern isolated features which may be due to uncontrolled fluctuations during the preparation process of the initial state.

5 Discussion

A constant magnetic field acts to stabilise the HS phase and shifts downwards the equilibrium temperature of the spin-crossover systems, *i.e.* the temperature T_{equ}. for which the HS and LS spin states are equipopulated. This shift will be denoted δT_{equ}, and it varies as $\sim B^2$ for symmetry reasons. In a crude first approach the thermal hysteresis loop is also shifted, as a whole, by the same amount $\delta T_{\mathrm{equ}}(B)$, because (i) the loop is $\sim$ centred around T_{equ} and (ii) the relative width of the loop mainly depends on the ratio: interaction parameter/equilibrium temperature (this ratio does not significantly change with the applied field). A more detailed analysis, based on the Ising-like model, is presently being made. It suggests that the descending branch of the thermal hysteresis loop is more shifted than the ascending one. This asymmetrical effect is due to the larger sensitivity of the HS metastable states to the magnetic field.

Following [6], the analytical expression for the field dependence of the equilibrium temperature is obtained from the magnetic free-energy expression (written in terms of molar quantities):

$$\begin{aligned}\Delta G &= G_{\mathrm{HS}} - G_{\mathrm{LS}}\\ &= \Delta H^{(0)} + (\chi_{\mathrm{HS}} - \chi_{\mathrm{LS}})\mu_0 H^2/2\\ &\quad + p\Delta V - T\Delta S^{(0)} - B\Delta M\\ &= \Delta H^{(0)} + p\Delta V - T\Delta S^{(0)} - (\chi_{\mathrm{HS}} - \chi_{\mathrm{LS}})B^2/2\mu_0 \end{aligned} \tag{1}$$

where $\Delta H^{(0)}$, $\Delta S^{(0)}$ refer to the properties of the system in absence of an external field. In the following, the pressure effect is neglected since $p \cong 0$, and the equilibrium temperature is deduced from $\Delta G = 0$, as:

$$\begin{aligned}T_{\mathrm{equ}}(B) &= \Delta H^{(0)}/\Delta S^{(0)} - (\chi_{\mathrm{HS}} - \chi_{LS})B^2/2\mu_0\Delta S^{(0)}\\ &= T_{\mathrm{equ}}(0) - (\chi_{\mathrm{HS}} - \chi_{\mathrm{LS}})B^2/2\mu_0\Delta S^{(0)}. \end{aligned} \tag{2}$$

Taking account of the paramagnetic properties of the spin-crossover systems, and substituting T_{equ} for the temperature in the Curie law, equation (2) becomes for spin states 0, S:

$$T_{\mathrm{equ}}(B) = T_{\mathrm{equ}}(0) - Ng^2S(S+1)(\mu_{\mathrm{B}}B)^2/6k_{\mathrm{B}}\Delta H^{(0)} \tag{3}$$

where μ_{B} is the Bohr magneton, g the Landé factor and k_{B} the Boltzmann constant. Equation (3) can also be obtained by a canonical approach of two-level systems ($g\mu_{\mathrm{B}} \ll k_{\mathrm{B}}T$); and takes the following form, for spin states 0, 2, with $g = 2$ (spin-only):

$$T_{\mathrm{equ}}(B) = T_{\mathrm{equ}}(0) - 4(\mu_{\mathrm{B}}B)^2/k_{\mathrm{B}}\Delta \tag{4}$$

with $\Delta = \Delta H^{(0)}/N_{\mathrm{A}}$ the energy gap of the two-level systems.

As explained below, we rather consider, in an isothermal process, the equivalent temperature shift:

$$\delta T_{\mathrm{isoth}} = T_{\mathrm{equ}}(0) - T_{\mathrm{equ}}(B) = +4(\mu_{\mathrm{B}}B)^2/k_{\mathrm{B}}\Delta. \tag{5}$$

With the value $\Delta \sim 1050$ K derived from calorimetric measurements [2], and for $B = 32$ T, the calculated temperature shift is $\delta T_{\mathrm{isoth}} \cong 1.8$ K.

Now let us state the simple *equivalence* between the present field-induced effect (δT_{equ}) and more familiar temperature-induced effects. Indeed, the behaviour of the system (in $T - n_{\mathrm{HS}}$ axes, for example) near the hysteresis loop is approximately governed by the *relative* position of the point representing the state of the system with respect of the hysteresis loop. Therefore, the effect of the field at constant temperature will be the same as the temperature shift $\delta T_{\mathrm{isoth}} = -\delta T_{\mathrm{equ}}$, at fixed thermal hysteresis loop. Here the subscript "isoth" recalls the isothermal character of the process. Actually, the proposed equivalence merely correlates the partial derivatives $\partial/\partial B$, $\partial/\partial T$ of the function $n_{\mathrm{HS}}(T, B)$, as suggested by the present experimental data.

Thus, for the present experiments, the 32 T field is equivalent to a temperature pulse which compares to the width of the thermal hysteresis loop. In the frame of an oversimplified description, assuming a quasi-static process, the triggering of a complete transition is expected. Clearly, the maximum observed effect, $\delta n_{\mathrm{HS}} \cong 0.15$, is somewhat smaller. Several reasons may be considered:

- the kinetic character of the process, which obviously dampens the response of the system;

- the shortcomings of the present crude model. Indeed, the brevity of the pulse makes the actual thermodynamic transformation of the sample closer to adiabatic [12] than isothermal. However, adiabatic magnetisation is expected to induce a transient increase in temperature, which should merely add up to the simple "isothermal" δT given by equation (5). Further improvements of the model are needed before a definitive conclusion can be made on this point.

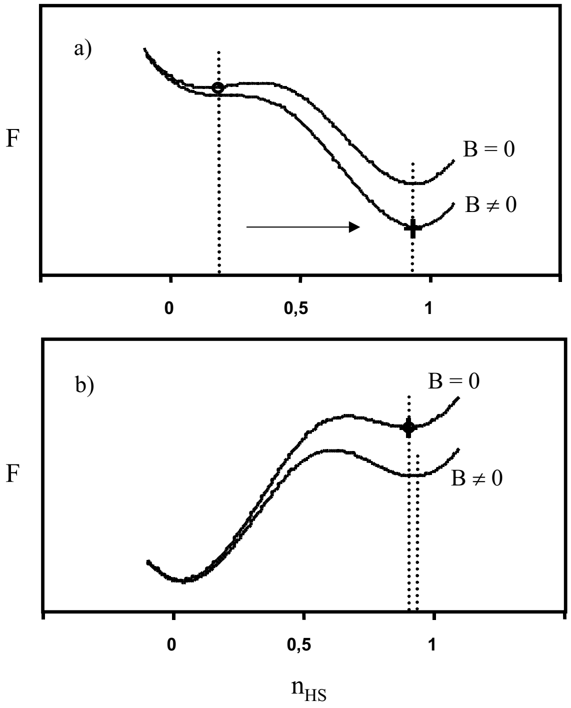

Fig. 5. The Landau free-energy associated with a first-order transition, for a system close to instability, in the ascending branch (a), $T > T_{\mathrm{equ}}$, and descending branch (b), $T < T_{\mathrm{equ}}$, of the thermal hysteresis loop. The full and dotted lines represent the free energy, respectively in presence and absence of the field. Initial and final states are shown by open circles and crosses, respectively.

The irreversible aspects of the process can be qualitatively understood on the basis of the (Landau) free-energy schemes associated with the first-order transitions, see Figure 5. For simplicity, we assume the sample is made up of independent crystallites with a distribution of transition temperatures, as in the classical Preisach model. The field mainly acts on the crystallites which initially are close to an unstable state, as shown in Figure 5: in the ascending branch of the hysteresis loop, Figure 5a, the field destabilises these states, and triggers the transition; on the contrary, in the descending branch, Figure 5b, the field stabilises these states, and the effect is reversible.

An alternative illustration of the irreversibility, taking advantage of the field/temperature equivalence, is shown in Figure 6. The properties in the quasi-static limit are described in terms of minor and major thermal hysteresis loops induced by the magnetic pulse. In the ascending branch, the pathway follows for some time the major loop and therefore leads to an irreversible change. On the contrary, in the descending branch, the pathway follows a minor loop, which is closed if the "wiping-out" property [11] is obeyed; indeed this property, typical for independent domains, has already been reported for the spin domains at the thermal transition [13,14]. Then, the effect induced on the descending branch can be expected to be reversible.

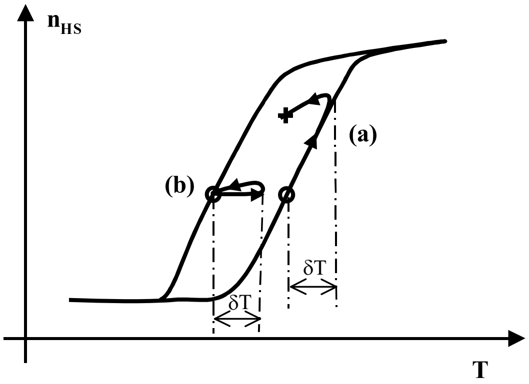

Fig. 6. A quasi-static description: the major thermal hysteresis loop, and the quasi-static paths associated with the equivalent temperature pulses, starting from the ascending (a) and descending (b) branches. Initial and final states are shown by open circles and crosses, respectively.

It is of interest to briefly discuss the kinetic aspects of the experiment. Indeed a quantitative analysis of the time dependence of response curves should be performed in terms of the kinetics of the physical processed involved in the experiment. As can be seen from Figure 5, the kinetics of the reversible and irreversible processes should differ basically (recent works relevant to the metastable states are listed in [15]):

(i) The reversible process only involves the usual LS ↔ HS relaxation time, associated with a small perturbation near the equilibrium state. An order of magnitude, at the considered temperature, is 50 ms (Fig. 3). This value does not seem to be unreasonable, according to the literature data. High- and low-temperature data can be found in [16–18]. In [18] the effect of cooperativity is evidenced, which makes the relaxation time a function of both the temperature and the HS fraction.

(ii) The irreversible process combines both the way up to the energy barrier (stochastic pathway) and the way down to the stable state (deterministic pathway). In other words the total evolution time of the process combines the lifetime of the metastable state, and the relaxation time. For this reason, the delay for the irreversible change (ascending branch) should be larger, as it is observed, ∼ 90 ms (Fig. 3).

A complete analysis of the kinetic triggering will probably involve a distribution of the energy barriers in the sample, and considering the rapid lowering of these barriers, as the magnetic field is increased. The analysis in terms of energy barrier distributions might be reminiscent of the "phonon spectroscopy" by means of pulsed field, which was reported some years ago for the relaxation of paramagnetic salts [19], with the static and dynamic effects deeply inter-related.

6 Conclusion

The use of intense magnetic field pulses, coupled with an optical detection system, has enabled us to observe the triggering of a spin transition, on the ascending branch of the thermal hysteresis loops, and $LS \leftrightarrow HS$ relaxation in the descending branch. The method should provide access to relaxation times in the time range of the pulse, and some insight into the role of energy barriers and lifetimes of the metastable states.

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