Original article

Triggering the spin-crossover of $Fe(phen)_2(NCS)_2$ by a pressure pulse. Pressure and magnetic field induce 'mirror effects'

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Abstract

We have studied the static and dynamic effects of pressure on the spin-transition in the temperature range of the thermal hysteresis loop for the compound $Fe(phen)_2(NCS)_2$. The high-spin fraction (n_{HS}) as a function of pressure and temperature has been determined by optical reflectivity. In this compound, the pressure was found to upward shift the spin-transition temperature by 23 K per kbar. During the dynamic pressure pulse, a decrease in n_{HS} is observed, with an irreversible (reversible) character in the descending (ascending) branch of the hysteresis loop. In this respect, pressure has a 'mirror effect' compared to the application of an intense and pulsed magnetic field, for which – as reported previously – an increase in n_{HS} is observed, with an irreversible (reversible) character in the ascending (descending) branch of the hysteresis loop. *To cite this article: A. Bousseksou et al., C. R. Chimie 6 (2003).*

Résumé

Nous avons étudié les effets statiques et dynamiques de l'application d'une pression sur le composé $Fe(phen)_2(NCS)_2$ dans son cycle d'hystérésis thermique. La fraction de l'état haut spin (n_{HS}) en fonction de la température et de la pression appliquée a été déterminée par mesure de la réflectivité optique. Dans ce composé, la pression a pour effet de déplacer la température d'équilibre du système vers les plus hautes températures, à raison de 23 K par kbar. L'application d'une impulsion de pression provoque une diminution irréversible (réversible) de n_{HS}, selon que le système se trouve sur la branche des températures décroissantes (croissantes) du cycle d'hystérésis. De ce point de vue, la pression induit un « effet miroir » comparé à celui du champ magnétique, puisque ce dernier – comme précédemment décrit – provoque une augmentation irréversible (réversible) de n_{HS}, selon que le système se trouve sur la branche des températures décroissantes (croissantes) du cycle d'hystérésis. *Pour citer cet article : A. Bousseksou et al., C. R. Chimie 6 (2003).*

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1. Introduction

Iron(II) complexes displaying spin-crossover (SCO) between the $^1A_1$ low-spin (LS) and the $^5T_2$ high-spin (HS) states have been the subject of much work during the last decades [1–4]. Beside fundamental research, there have been several proposals for the design of information processing devices (e.g., memories, displays, etc.) based on SCO compounds. For example, the discovery of the LIESST (light induced excited state spin trapping) effect suggested that the SCO complexes could be used as optical switches [5, 6]. However, the LIESST phenomenon has been observed only at very low temperatures, typically below 80 K.

Another interesting approach to build memory devices from SCO materials is based on the fact that the thermal spin transition may occur with hysteresis loop, conferring a memory effect to these systems [7, 8]. Indeed, inside the temperature range of the hysteresis loop, the spin state of the system depends on its history, hence on the information that has been stored. Since the optical and magnetic properties of the material are markedly different in the two spin states, this information can be read easily by optical or magnetic means. Of course, the ideal situation is when the hysteresis cycle is centred on room temperature (RT). The first spin-crossover complex with large and abrupt thermal hysteresis loop around RT was reported in 1993 in conjunction with optical reading and thermal addressing of the stored information [9]. This report has been followed by an intense research for compounds with RT hysteresis, and today several examples are known [10]. Besides thermal addressing, switching of spin-states by short magnetic [11–15] and light pulses [16, 17] in the thermal hysteresis interval has also been investigated recently. However, reports on different possibilities for addressing these systems in the hysteresis loop are still rather scarce and the kinetic aspects (transition rates, macroscopic barrier heights, etc.), which have a foremost importance in the writing and erasing processes, are yet little characterized.

Concerning the magnetic field effects on the compound $Fe(phen)_2(NCS)_2$, the main findings can be summarized as follows [11]. Following a 1-s pulsed magnetic field of 32 T, sizeable changes are observed in the HS fraction. In the temperature range of the hysteresis loop, an increase in n_{HS} is obtained, with an
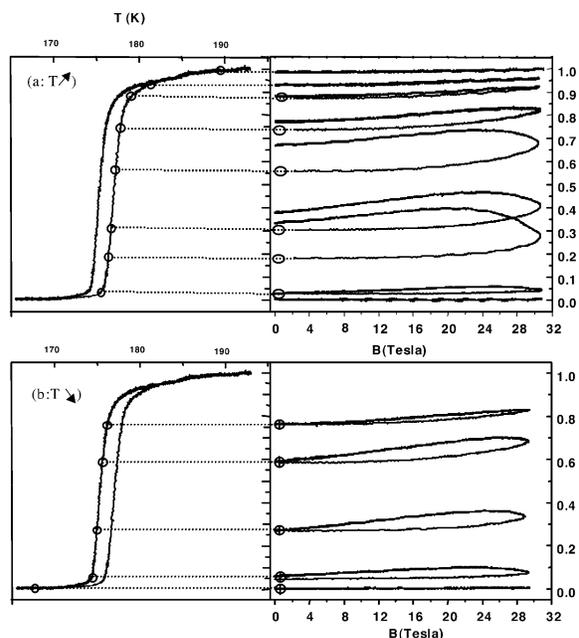
Fig. 1. Effect of a pulsed magnetic field on the high-spin fraction of $Fe(phen)_2(NCS)_2$ in the ascending (a) and descending (b) branches of the thermal hysteresis loop (after [11]).

irreversible (reversible) character in the ascending (descending) branch of the loop (Fig. 1). A quasi-static magnetic field of 32 T theoretically corresponds to a variation of the spin-transition temperature ($T_{1/2}$) – defined as the temperature for which $n_{HS} = \frac{1}{2}$ – by 1.8 K toward the lower temperatures. However, the actual response of the system (~15% of LS molecules are converted to the HS state) was found smaller than expected from theory, probably due to kinetic barriers in the system. An important point comes out from the experimental data concerning the delay between the excitation (magnetic field) and the response (increase of n_{HS}). For the ascending and descending branches, markedly different delays have been observed: 90 and 50 ms, respectively, which definitely indicates the kinetic character of the triggering process.

In this paper, we report on the effects of a *pressure pulse* in the thermal hysteresis loop of $Fe(phen)_2(NCS)_2$. It is well known that an external pressure stabilizes the state with smaller volume (LS state) in contrast to magnetic field, which stabilizes the state with higher spin (HS state). For relatively small applied pressures (up to 1000 bar) the work term, $p\,\Delta V$, to the Gibbs' free energy is already significant because

of the large difference in volume ($\Delta V_{HL} = V_{HS} - V_{LS}$) between the HS and LS forms [2,4]. Indeed, the spin equilibrium as well as the HS to LS relaxation in SCO complexes was generally found to be very sensitive to external pressure. For example, $T_{1/2}$ was found to shift by as much as 20–30 K/Kbar in several SCO compounds [18–20].

The compound $Fe(phen)_2(NCS)_2$, which we have selected for this study, has been extensively investigated under quasi-static pressure [21–27]. Under atmospheric pressure, it undergoes an abrupt spin-crossover around 176 K, with a hysteresis of ~1.3 K [11]. At room temperature, under hydrostatic conditions, the HS form can be converted into the LS form by application of high pressure. No change in space group has been observed during this transformation [26]. Concerning the transition pressure ($p_{1/2}$), there are some discrepancies in the literature due to the polymorphism of this compound and also because of possible non-hydrostatic conditions. According to the thorough analysis of Roux et al. [27], polymorphs I and II exhibit SCO around 8 and 6.5 kbar, respectively. There are also different observations concerning the completeness of the transition under pressure, but under truly hydrostatic conditions it appears to be quasi-complete (< 10 % HS residue). It should also be noted that subsequent pressure cycles up to 15 kbar led to the irreversible alteration of the transition curve [27], while pressurization up to 10 kbar had no apparent effect on the spin transition curves [25]. The only pressure experiments conducted under cryogenic temperatures on this compound were reported by Usha et al. [25]. From the analysis of their magnetic susceptibility isobars they have obtained a quasi-linear shift of $T_{1/2}$ as a function of the applied pressure, the shift being 22 (± 1) K per kilobar.

2. Experimental

The sample of $Fe(phen)_2(NCS)_2$ (polymorph I) has been prepared as described in [28]. The variable temperature, hydrostatic pressure system (He gas) and the optical reflectivity (550 ± 50 nm bandpass filter) detection device have been described in [29]. The ratio I_R/I_0 (reflected light intensity/incident light intensity) was monitored continuously, while pressure and temperature were governed independently. The stability of temperature was better than ± 0.1 K, while the pressure
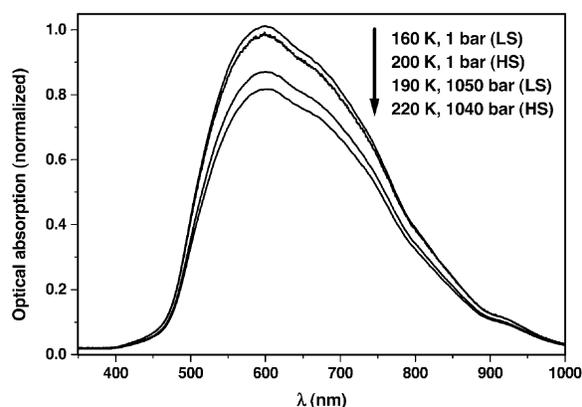
Fig. 2. Optical absorption spectra of $Fe(phen)_2(NCS)_2$ at some selected temperatures and pressures illustrating the importance of correction factors applied on reflectivity data.

could be stabilized within ± 5 bar. According to previous studies [11], the I_R/I_0 ratio follows quite linearly the variation of n_{HS}. Corrections were, however, necessary because small pressure effects on I_R/I_0 are present even in the absence of any spin state change. These effects are mainly due to change of optical properties of the pressure cell, and, to a lesser extent, to the shift (in intensity as well as in wavelength) of the optical absorption bands under pressure. Correction factors were obtained by recording LS and HS absorption spectra (300–1000 nm) at different pressures in the two spin states (Fig. 2).

It is worth noting that reflectivity enables the investigation of the sample 'surface', hence the reflectivity data do not necessarily match those obtained by 'bulk methods' such as magnetic measurements [30]. Finally, one should also be aware that the thermocouple is placed relatively far from the sample (outside the pressure cell), leading to a small difference between the real and the displayed temperature (~3 K). This feature does not affect, however, the precision (i.e. the resettability) of temperature.

3. Results and discussion

Spin transition curves of $Fe(phen)_2(NCS)_2$ have been recorded at 1, 200 and 1030 bar as a function of T. As an example, Fig. 3 shows two successive temperature loops at 200 kbar, revealing a good reproducibility of the measurements. Alternatively, a pressure loop has also been recorded in isothermal conditions at 195 K
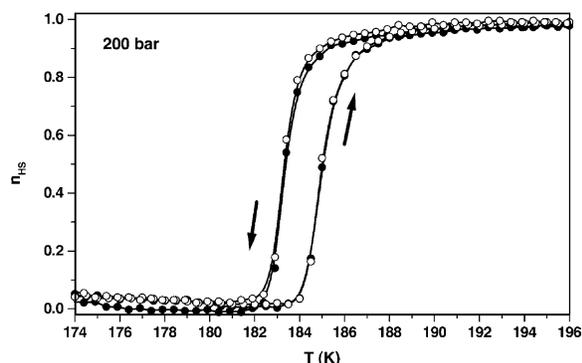
Fig. 3. Successive thermal hysteresis loops of Fe(phen)$_2$(NCS)$_2$ at 200 bar (lines are inserted to guide the eye).

(Fig. 4). Based on these measurements, the *p–T* phase diagram of the spin states could be established (Fig. 5). A linear fit leads to the variation dT/dp = 23 (± 0.4) K kbar^{-1}, in excellent accord with the results of Usha et al. [25]. The slope is somewhat steeper for the line $T_{1/2}\downarrow$ compared to $T_{1/2}\uparrow$, in agreement with the mean-field theory [19], but the difference (0.8 K kbar^{-1}) remains close to the experimental precision. Fig. 5 suggests also a tight relationship between pressure and temperature loops. Indeed, following the simple two-level analysis of [20], we could derive the shape of the isothermal loop from that of the isobaric loops; the computed shape is in good agreement with the experimental one.

As explained in [20], the pressure dependence of the equilibrium temperature is expected to be linear:

$$\mathrm{d}T_{1/2}(p)/\mathrm{d}p = \Delta V_{\mathrm{HL}}/\Delta S_{\mathrm{HL}} \qquad (1)$$
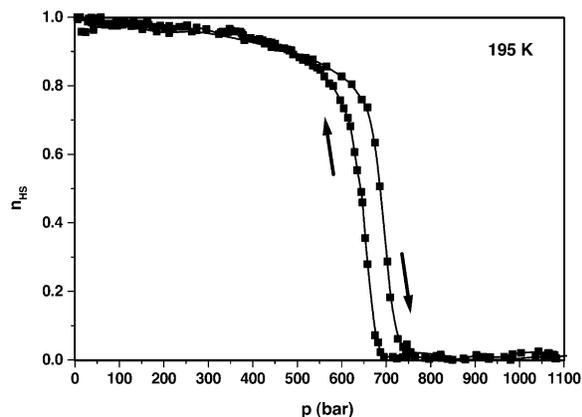
Fig. 4. Pressure hysteresis loop of Fe(phen)$_2$(NCS)$_2$ at 195 K (lines are inserted to guide the eye).
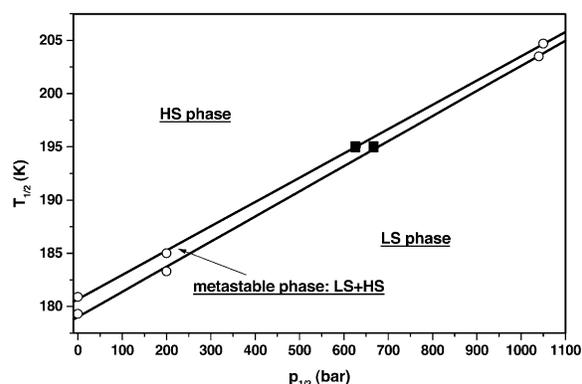
Fig. 5. The (*p*,*T*) phase diagram of Fe(phen)$_2$(NCS)$_2$ from isobaric thermal hysteresis loops (○) and from isothermal piezo hysteresis loops (■). The straight lines represent linear fit on the data.

Then, from the experimental ΔS_{HL} value of 49 J K^{-1} mol^{-1}[31] – neglecting the small pressure dependence of the ratio $\Delta V_{\mathrm{HL}}/\Delta S_{\mathrm{HL}}$ –, one can obtain a volume variation (ΔV_{HL}) of ~19 Å^3 per molecule, in excellent agreement with the value of 18 Å^3 per molecule calculated from variable-temperature X-ray diffraction data (at ambient pressure) [26].

We also carried out a series of pulsed pressure measurements. The pressure pulses (up to 300 bar) were applied at different temperatures in the hysteresis loop. Before each measurement in the ascending (descending) branch of the hysteresis loop, the sample was reset at 150 K (200 K). After setting the desired temperature, 10 min were allowed for the sample to reach complete thermal stability, and then the pressure pulse was applied. The maximum pressure is reached in ~5 min and then decreased to 1 bar in ~5 min, but it should be noted that, in the present state of the device, the pressure is controlled manually, thus the shape of the pulse is not completely reproducible. Fig. 6 shows a typical pulsed pressure experiment (50 bar, 180.3 K) in the descending branch of the thermal spin-transition curve. It can be seen that the n_{HS} fraction decreases with increasing pressure, but when releasing the pressure the system does not return completely to its initial state. The complicated variation of the n_{HS} fraction upon decompression is of course related to the shape of the pressure pulse. We shall see later that the experiment contains a kinetic aspect, which also should be reflected in the shape of the response of the system.

In Fig. 7, the effect of a 50 bar pressure pulse is compared for the ascending and descending branches
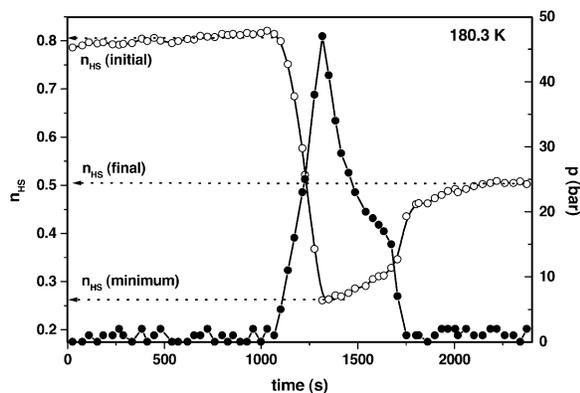
Fig. 6. A typical pulsed pressure experiment in the *descending* branch of the thermal hysteresis loop showing the time dependence of the pressure pulse (•) and the n_{HS} fraction (○) (lines are inserted to guide the eye).
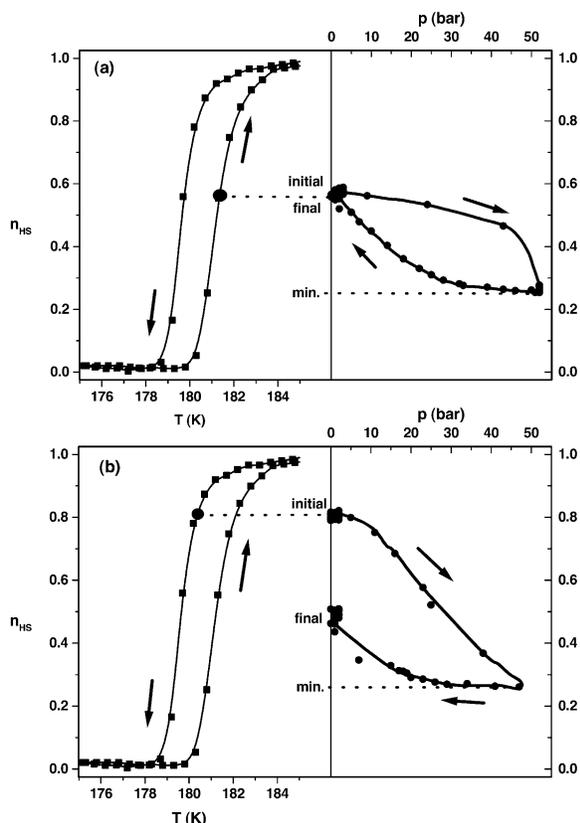
Fig. 7. Pressure effect on the high spin fraction in Fe(phen)$_2$(NCS)$_2$ in the ascending (**a**) and descending (**b**) branches of the thermal hysteresis loop (lines are inserted to guide the eye).

of the hysteresis loop. These figures show that a sizeable triggering of the spin transition is obtained for both branches. However, in the descending branch, the *irreversible* decrease of n_{HS} is evidenced by the observation over a rather long time (10–15 min), while the drop of n_{HS} appeared to be completely *reversible* in the ascending branch.

We now discuss the amplitudes of spin conversion. The data obtained for different pressures and initial n_{HS} values in the ascending and descending branch of the hysteresis loop are listed in Table 1. Due to the somewhat arbitrary form of the pressure pulses, only a qualitative comparison can be made. It appears, however, clearly that the variation of n_{HS} is always reversible (irreversible) in the ascending (descending) branch and these variations (both the reversible and irreversible ones) are proportional to pressure.

In a simplified approach [20], one can consider the effect of the pressure pulse to be equivalent to a temperature-induced effect [11]. Actually, this equivalence merely correlates the partial derivatives $\partial/\partial p$, $\partial/\partial T$ of the function $n_{HS}(T,p)$, as suggested by the present experimental data. It is interesting thus to note that – compared to the temperature shifts that can be expected from the $dT(p)/dp$ slope of the phase diagram – the experimentally observed response of the system is attenuated. For example, 50 bar correspond (theoretically) to a shift of 1.15 K in the transition temperature, thus it should trigger a quasi-complete and irreversible spin conversion for any initial n_{HS} value in the

Table 1
Experimental values of the amplitudes of spin conversion for different pressures and initial n_{HS} values in the ascending and descending branches of the hysteresis loop.

	n_{HS} initial	n_{HS} minimum	n_{HS} final	Δp (bar)
$T\uparrow$	0.4	0	0.4	50
	0.55	0.1	0.55	50
	0.6	0.25	0.6	50
	0.7	0.4	0.7	50
	1	0.6	1	50
	0.75	0.15	0.75	100
	0.75	0.10	0.75	220
	0.75	0	0.75	300
$T\downarrow$	0.2	0.1	0.15	50
	0.80	0.25	0.5	50
	0.75	0.1	0.4	110
	0.75	0.05	0.05	220

descending branch of the hysteresis loop. Contrary to this expectation, only a partial triggering was achieved even with a 110-bar pulse (Table 1). Such a discrepancy between (quasi-)static theory and dynamic experiments has already been evidenced in pulsed magnetic field measurements and was related to the kinetic aspects of the process [11,14]. As explained in [15], a relatively slow relaxation may account for the attenuation of the response and also its time delay.

4. Conclusions

The present pulsed pressure experiments revealed properties symmetrical of our earlier pulsed magnetic field experiments: The pressure and magnetic field induce 'mirror' effects. While an applied magnetic field stabilizes the HS state via the Zeeman effect, external pressure stabilizes the LS state due to the work term. Therefore, a pressure (magnetic) pulse results in an irreversible decrease (increase) of n_{HS} in the descending (ascending) branch of the thermal hysteresis cycle, whereas these changes are always reversible in the ascending (descending) branch (Figs. 1 and 7). If one compares the theoretical shift of the transition temperature under quasi-static external pressure and magnetic field in the case of $Fe(phen)_2(NCS)_2$, it appears that the effect of 1 T is roughly the opposite of the shift caused by 2.5 bar!

The fact that such small pressure as 200 bar triggered a quasi-complete crossover between the two spin-states suggests that piezo effects might be implemented in devices for addressing SCO materials. Further experiments are in progress to better control and understand the dynamical aspects of the pressure induced spin-state switch. A possible issue will be the comparison to the pressure minor hysteresis loops [32], which can be obtained in quasi-static regime.

Acknowledgements

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