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Two-level Ising-like model for spin-crossover phenomenon including the magnetic field effect: the mean-field approximation and Monte Carlo resolutions

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Dedicated to Patrick Cassoux on the occasion of his retirement

Abstract

In this paper we analysed the magnetic field effect on the spin-crossover phenomenon using different theoretical approaches: thermodynamic and Ising-like models. This latter, including magnetic field, was treated in the mean-field approximation and—for the first time—by Monte Carlo numerical method. We propose an adaptation of the metropolis algorithm to take into account the different degeneracies of the high and low-spin levels and their Zeeman splitings due to the effect of magnetic field in both states. A comparison of both methods is given and discussed.

Keywords: Spin-crossover; Bistability; Magnetic field effect; Ising-like model; Monte Carlo

1. Introduction

In certain transition metal complexes, the spin state of the central metal ion can be altered under external perturbations, such as temperature, pressure, light or magnetic fields [1–4]. These spin-crossover (SC) complexes, displaying thermo-, photo- and piezo- and magneto-chromic properties, are of growing importance in the area of functional materials, especially for application in memory and display devices and as molecular switches [5].

Concerning the magneto-chromic properties, it is well known that the application of a magnetic field stabilizes the high-spin (HS) state over the low-spin (LS) state and therefore shifts the thermal SC to lower temperatures. Sasaki and Kambara using ligand field calculations [6] predicted this effect and its magnitude. The first experimental study using a static magnetic field of 5.5 T was reported by Qi et al. [7]. They observed a -0.1 ± 0.04 K shift of the transition temperature ($T_{1/2}$) for the complex $Fe(phen)_2(NCS)_2$. Latter, further complexes with Co^{III} [8], Fe^{II} [9] and Mn^{III} [10] central ions were investigated under somewhat higher static fields (10–23 T). In all cases, small shifts in $T_{1/2}$ (from -0.1 to -1.6 K) were detected. The static magnetic field effect on the dynamical processes has also been considered [11,12].

Recently, we have reported the effect of a pulsed magnetic field (PMF) on the SC systems $Fe(phen)_2(NCS)_2$ [13], $Fe_xNi_{1-x}(btr)_2(NCS)_2 \cdot H_2O$ (with $x = 0.33$, 0.52 or 0.8) [14,15] $Co(H_2(fsa)_2en)py_2$ [4]. The main findings can be summarised as follows:

(i) Applying a 1 s PMF of 32 T to the spin transition solid $Fe(phen)_2(NCS)_2$, sizeable effects are observed on the HS fraction. In the hysteresis loop temperature range, an increase of 15% in the HS fraction is obtained, with an irreversible (reversible) character in the ascending (descending) branch of the loop [13]. The time dependence of the HS fraction provides information on

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the kinetics of the SC process at the spin transition. Delays between the excitation (magnetic field) and the response (increase of the HS proportion) have been observed: 90 ms (50 ms) in the ascending (descending) branch.

(ii) Applying a PMF of 32 T to the solid $Co^{II}(H_2(fsa)_2en)py_2$ leads to an irreversible and quasi-complete $S = 1/2 \rightarrow S = 3/2$ transition [4]. The effects are shown in Fig. 1.

(iii) A correlation between the delay (excitation/response) and the cooperativity of the SC phenomenon has been evidenced by studying the effect of PMF on the family of diluted complexes $Fe_xNi_{(1-x)}(btr)_2(NCS)_2 \cdot H_2O$ [15] where the dilution x controls the cooperativity. An exponential dependence between the delay (excitation/response) and the cooperativity has been evidenced. This dependence is shown on Fig. 2.

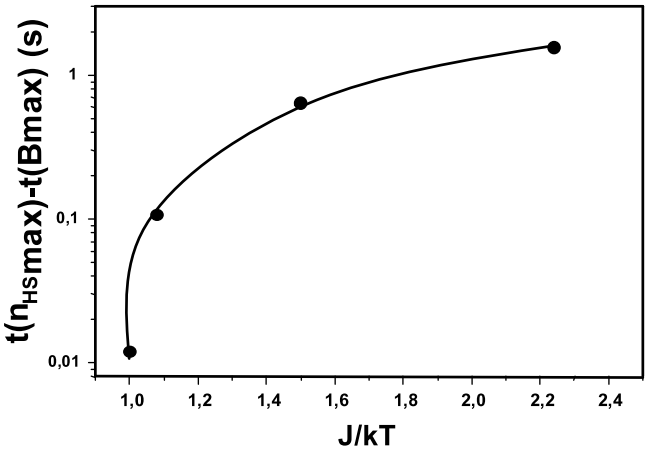

Fig. 2. The time separation between $B^{max}(t)$ and $n_{HS}^{max}(t)$ on the ascending branch of the hysteresis loop (for initial temperatures corresponding to a molecular fraction $n_{HS}^0 = 0.4$) for different samples as a function of J/k_BT_c (after [15]).

In the present paper we study theoretically the effect of magnetic field on the SC phenomenon by using the Ising-like model adapted to the effect of magnetic field and resolved by the mean-field approximation and Monte Carlo techniques. SC between a diamagnetic $S = 0$ and a paramagnetic $S = 2$ (Iron(II) complexes) and also between two paramagnetic states $S = 1/2$, $S = 3/2$ (cobalt complexes) are examined.

2. Theoretical models

2.1. Two level Ising-like model

To describe a system with two energy levels, a fictious spin σ is associated with the HS and LS states for each molecule i. Then, the energy of the system is expressed as a function of the energy gap (Δ_0) between the two levels of an isolated molecule and a phenomenological parameter (J_{ij}) describing the interactions between the molecules i and j [16]:

$$\widehat{\mathbf{H}} = \frac{\Delta_0}{2}\widehat{\sigma_i} + \sum_{j \neq i} J_{ij}\widehat{\sigma_i}\widehat{\sigma_j} \tag{1}$$

where $\widehat{\sigma}$ is a fictious spin operator with eigen values $+1$ 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.

The magnetic field, via the Zeeman effect, removes the electronic degeneracies of the HS and LS levels, and the new Hamiltonian is written as:

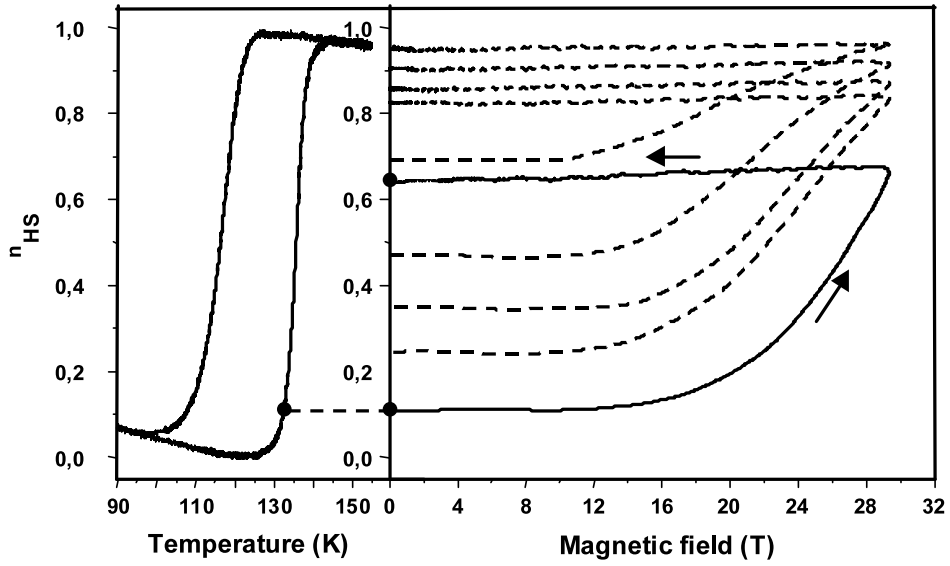

Fig. 1. Set of isotherms $n_{HS}(B)$ showing the irreversible (and quasi-total) triggering effect on the HS fraction in $Co(H_2(fsa)_2en)(py)_2$ for an applied PMF in the metastable LS state (after [4]).

$$\widehat{\mathbf{H}}_i = \frac{\Delta_0}{2}\widehat{\sigma_i} + \sum_{j\neq i} J_{ij}\widehat{\sigma_i}\widehat{\sigma_j} + g_L\mu_B B\widehat{S_z}\frac{\widehat{\sigma_i}+1}{2} \quad (2)$$

where μ_B is the Bohr magnetron, g_L is the Landé factor, B is the magnetic field strength and S_z is the projection of the spin moment operator along the field direction. This latter can take any of the $2S+1$ values $S_z = -S, -S+1, \ldots, S$. The system is described now by its spin state σ_i and also by S_z.

2.2. The mean-field approximation

In order to solve analytically the Hamiltonian (Eq. (2)), we use the mean-field approximation where the interaction-energy of the neighbouring molecules is averaged as $J\langle\widehat{\sigma}\rangle$:

$$\sum_{j\neq i} J_{ij}\widehat{\sigma_i}\widehat{\sigma_j} \rightarrow J\langle\widehat{\sigma}\rangle\widehat{\sigma_i} \quad (3)$$

In this approximation, we can deduce the HS fraction n_{HS} through the average of the fictious spin $\langle\widehat{\sigma}\rangle$:

$$n_{HS} = \frac{\langle\widehat{\sigma}\rangle + 1}{2} \quad (4)$$

as well as the transition temperature ($T_{1/2}$), defined as the temperature for which the proportions of LS and HS molecules are equal ($n_{HS} = n_{LS} = 1/2$). By expliciting the mean value of $\widehat{\sigma}$ we obtain for n_{HS}:

$$n_{HS}(B) = \frac{r(B)}{r(B) + \exp\dfrac{\Delta_0 - 2J(2n_{HS}-1)}{k_B T}} \quad (5)$$

with

$$r(B) = \frac{g_{HS,vib}\, g(B, S_{HS})}{g_{LS,vib}\, g(B, S_{LS})}$$

and

$$g(B,S) = \frac{\sin h((2S+1)g_{L\mu B}B/2k_BT)}{\sin h(g_{L\mu B}B/2k_BT)}$$

and for $T_{1/2}$:

$$T_{1/2} = \frac{\Delta_0}{k_B \ln\left\{\dfrac{g_{HS,vib}}{g_{LS,vib}}\dfrac{\sin h\left[\dfrac{(2S_{HS}+1)g_L\mu_B B}{2k_B T_{1/2}}\right]}{\sin h\left[\dfrac{(2S_{LS}+1)g_L\mu_B B}{2k_B T_{1/2}}\right]}\right\}} \quad (6)$$

where $g_{HS,vib}$ and $g_{LS,vib}$ are the vibrational degeneracies of the HS and LS states, respectively.

In contrast to [10], the exact solution of the self-consistent Eqs. (5) and (6) can be obtained only numerically! Fig. 3 represents the resolution of Eq. (5), for each fixed temperature, using the Newton numerical method. This resolution was carried out in the case of a gradual conversion between the diamagnetic ($S_{LS} = 0$) and the paramagnetic ($S_{HS} = 2$) spin states with the parameter set $\Delta_0 = 700$ K, $J = 139$ K, $g_{HS,vib}/g_{LS,vib} = 30$ and for different strengths of the applied magnetic field. One can note that for an applied magnetic field above 18 T, a first order phase transition appears accompanied by a thermal hysteresis. This effect has been also shown qualitatively in Ref. [10]. In fact, the magnetic field decreases the transition temperature, but the condition for a first-order transition $J/k_BT_c > 1$ [17] remains unchanged. This condition is illustrated on Fig. 4. For $J = 139$ K the first order phase transition appears above 138.88 K.

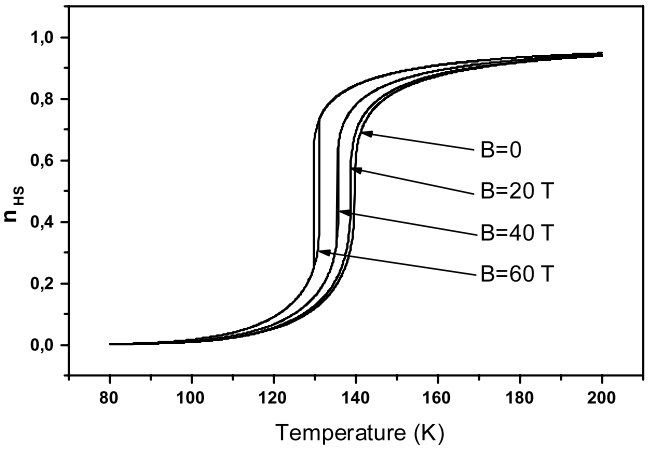

Fig. 3. Calculated Spin transition curves for different magnetic field strengths; with $S_{LS} = 0$, $S_{HS} = 2$, $\Delta_0 = 700$ K, $J = 139$ K, $g_{HS,vib}/g_{LS,vib} = 30$ with the Ising-like model solved by the mean-field approximation.

As described in Refs. [13,14], see also [6–8], we can also obtain an analytical expression for the variation of $T_{1/2}$ as a function of the applied magnetic field strength from the Landau free energy in presence of a field and in thermodynamic equilibrium:

$$\delta T_{1/2} = -\frac{4(\mu_B B)^2}{k_B \Delta_0} \quad (7)$$

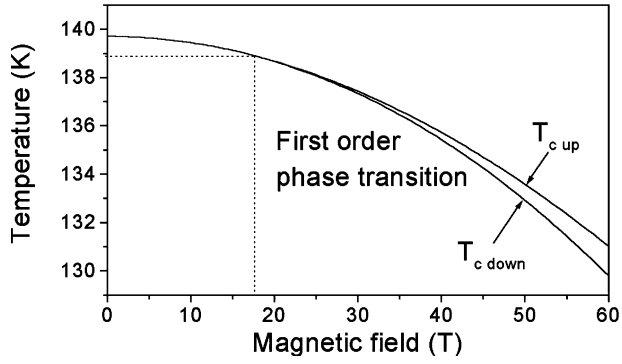

Fig. 4. Variation of spin transition temperature (in heating and cooling mode) as a function of the magnetic field strength; with $S_{LS} = 0$, $S_{HS} = 2$, $\Delta_0 = 700$ K, $J = 139$ K, $g_{HS,vib}/g_{LS,vib} = 30$.

for the case when $S_{LS} = 0$ and $S_{HS} = 2$

$$\delta T_{1/2} = -\frac{2(\mu_B B)^2}{k_B \Delta_0} \tag{8}$$

for the case when $S_{LS} = 1/2$ and $S_{HS} = 3/2$.

Fig. 5 represents Newton numerical resolution of Eq. (6) using the same parameter set and for increasing values of the magnetic field strength. On the same figure the result of the thermodynamic approach (Eq. (7)) is shown too. It appears, as expected, that the transition temperature decreases quadratically with the magnetic field B, and the two approaches are equivalent for weak magnetic fields, but they diverge for strong fields.

For the case of $Co(H_2(fsa)_2en)py_2$ ($S_{LS} = 1/2$ and $S_{HS} = 3/2$), the self-consistent Eq. (6) reduces to:

$$T_{1/2} = \frac{\Delta_0}{k_B \ln\left[2\frac{g_{HS,vib}}{g_{LS,vib}} \cosh\left(\frac{2\mu_B B}{k_B T_{1/2}}\right)\right]} \tag{9}$$

Fig. 6 shows the difference between the zero-field transition temperature $T_{1/2}(B = 0)$ and the transition temperature for an applied magnetic field $T_{1/2}(B)$, using $\Delta_0 = 168$ K and $g_{HS,vib}/g_{LS,vib} = 1.875$ determined from calorimetric measurements [18]. A static magnetic field of 30 T corresponds in this case to a variation of $T_{1/2}$ by 4.9 K towards the lower temperatures. This value is in perfect agreement with that obtained in Ref. [4].

2.3. Monte Carlo method

The mean-field approximation is not well adapted to determine the exact value of the hysteresis loop, even if this method is powerful for understanding the main ingredients of the SC phenomenon [16,19,20].

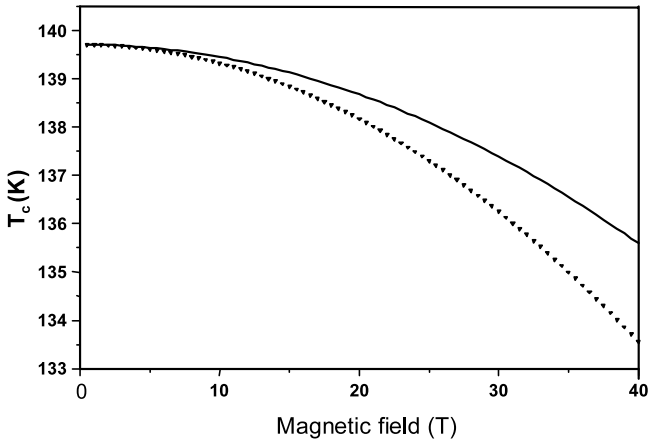

Fig. 5. Variation of the spin transition temperature as a function of the magnetic field strength; with $S_{LS} = 0$, $S_{HS} = 2$, $\Delta_0 = 700$ K, $J = 139$ K, $g_{HS,vib}/g_{LS,vib} = 30$, calculated using Eq. (6) (full line) and Eq. (7) (triangles).

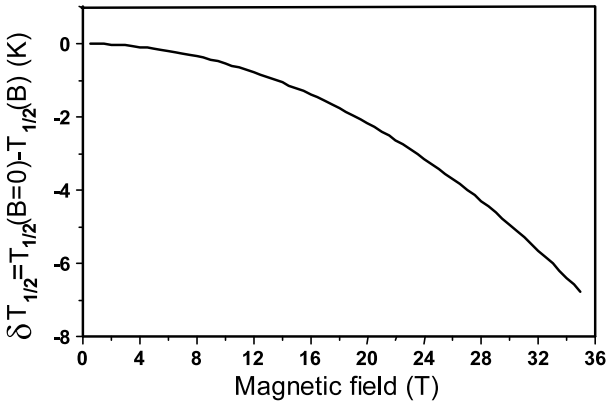

Fig. 6. $Co(H_2(fsa)_2en)py_2$, Numerical calculation of the variation of the spin transition temperature as a function of the static magnetic field strength, using the two-level Ising-like model with the mean-field approximation.

We have thus used, as suggested in Ref. [20], the Monte Carlo–Metropolis method [21,22] to solve statistically the Hamiltonian (Eq. (1)) as described in Refs. [23,24]. The application of a static magnetic field leads to the splitting of the electronic degeneracies, thus the algorithm Metropolis must be modified to solve the Hamiltonian (Eq. (2)). Let us consider a transition for a complex with Fe^{II} ($S_{LS} = 0$, $S_{HS} = 2$). There are five possible transitions (noted from 1 to 5), and the detailed balance of equilibrium is written as:

$$g_{vib,HS} \sum_{i=-2}^{2} e^{-\beta E_{HS_i}} W_{HS_i \to LS} = g_{vib,LS} e^{-\beta E_{LS}} \sum_{i=-2}^{2} W_{LS \to HS_i} \tag{10}$$

where g_{vib} is the vibrational degeneracy, $\beta = 1/T$, E the energy and W transition rate.

The algorithm considers only one transition each time hence when a spin j flips from the $-\sigma_j$ to $+\sigma_j$; one must know which probability is to consider. For this, we have introduced a second random number, which decides at each iteration, to which HS state the system converts. It should be noted also, that in our calculation the time-unit is the Monte Carlo loop. On the other hand, the time unit for the transition rate $W_{LS \to HS}$ is not a loop, but five loops because of the second random number. In order to have the same time reference, we divide $W'_{LS \to HS_i}$ by five. The equilibrium condition used by the algorithm becomes:

$$g_{vib,HS} e^{-\beta E_{HS_i}} W_{HS_i \to LS} = g_{vib,LS} e^{-\beta E_{LS}} \frac{W'_{LS \to HS_i}}{5} v \tag{11}$$

with $i = -2, -1, 0, +1, +2$.

The sum of the five equations used by the algorithm confirms well the detailed balance condition (Eq. (10)).

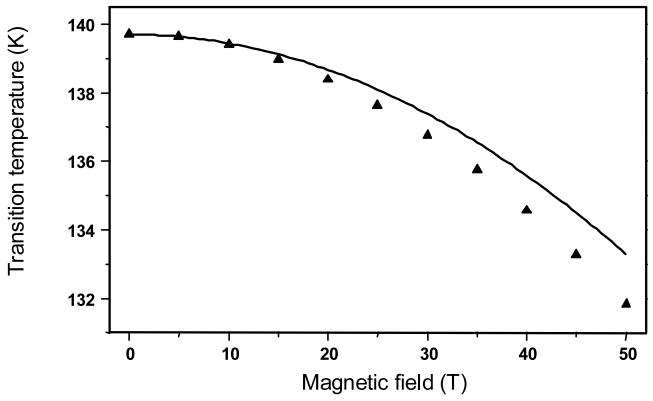

Fig. 7. Calculated spin transition temperature as a function of the magnetic field strength, with $S_{LS} = 0$, $S_{HS} = 2$, $\Delta_0 = 700$ K, $J = 120$ K, $g_{HS,vib}/g_{LS,vib} = 30$, using the two-level Ising-like model. Mean-field approximation (full line) and Monte Carlo resolution (triangles).

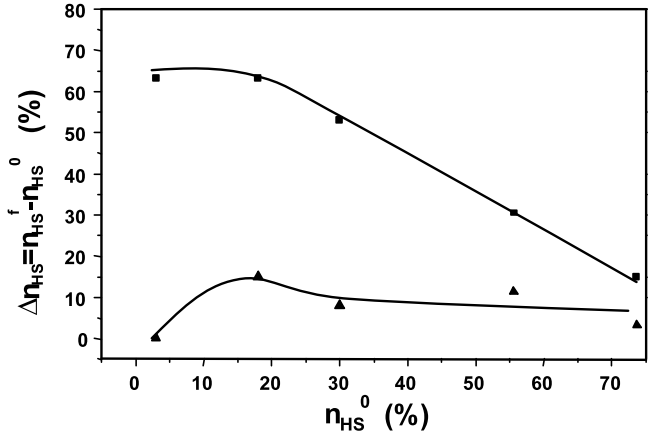

Fig. 8. $Fe(phen)_2NCS_2$, comparison of the triggering amplitudes by 32 T, as function of the HS fraction of the initial state. Experimental data (triangles) and calculation using the quasi-static approach (squares).

Fig. 7, shows the variation of $T_{1/2}$ as a function of the static magnetic field in case of a gradual transition ($S_{LS} = 0$, $S_{HS} = 2$), for $\Delta_0 = 700$ K, $g_{HS,vib}/g_{LS,vib} = 30$ and $J = 120$ K, using the Monte Carlo method (triangles) and the mean-field approximation (straight line).

Bousseksou et al. [13] have shown that if the transition is supposed to be quasi-static, a magnetic pulse of 32 T is equivalent with a temperature pulse of 1.8 K for the complex $Fe(phen)_2NCS_2$. In the case of the complex $Co(H_2(fsa)_2en)py_2$, a pulse of 30 T was found to be equivalent with a temperature pulse of 4.9 K [4]. Fig. 8 compares the amplitudes of spin conversions induced by the magnetic field in $Fe(phen)_2NCS_2$ obtained experimentally and those obtained by the quasi-static approach. The same comparison is displayed in Fig. 9 for $Co(H_2(fsa)_2en)py_2$. In the case of $Fe(phen)_2NCS_2$, the actual response of the system is lower than expected from the quasi-static approach, while for the $Co(H_2(fsa)_2en)py_2$, the theory is in good agreement with the obtained results. This difference between the two systems is related to the kinetic aspects of the process. Hauser [25] have shown that the relaxation HS → LS relaxation depends on the temperature and n_{HS}. This relaxation depends inherently on the energy barrier which separates the two spin states and reduces the effect of the magnetic field. In the case of $Fe(phen)_2NCS_2$ a relatively slow relaxation may explain the delay between the excitation and the response as well as the attenuation of the response in comparison with the magnetic field strength. One can qualitatively appreciate the relaxation rate by measuring the variation of the thermal hysteresis width as a function of the applied heating/cooling rate. The strong variation of the hysteresis width for rates between 0.2 and 10 K min^{-1}

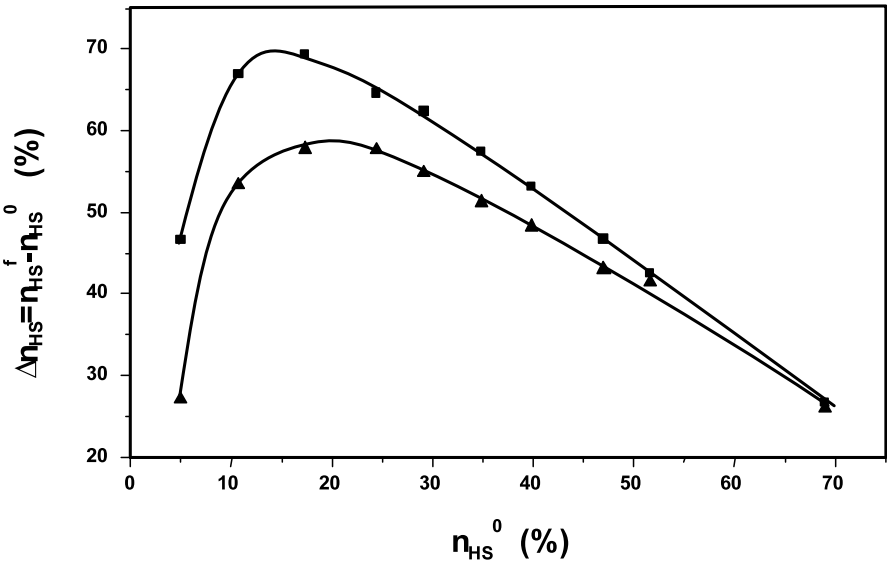

Fig. 9. $Co(H_2(fsa)_2en)py_2$, comparison of the triggering amplitudes by 32 T, as function of the HS fraction of the initial state. Experimental data (triangles) and calculation using the quasi-static approach (squares).

[26] shows that the relaxation is rather slow in this case. In addition the cooperativity of the system can modulate the delay excitation/response, in regards of the experiments carried out with the $Fe_xNi_{(1-x)}$ complexes [15]. On the other hand, for the $Co(H_2(fsa)_2en)py_2$, the relaxation is supposed to be faster, i.e. the barrier height is lower compared to the Fe^{II} complex. This could explain that no delay was observed between the magnetic pulse maximum and the minimum of the HS fraction as well as the good agreement between the experimental and calculated amplitudes of the spin transition. This hypothesis is supported by the reproducibility of the thermal loops when the heating rate was varied between 0.2 and 20 K min^{-1}. A firmer confirmation could be obtained by measuring the HS → LS relaxation rates. These experiments are in progress.

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