

Communication

# Multi-Step in 3D Spin Crossover Nanoparticles Simulated by an Ising Model Using Entropic Sampling Monte Carlo Technique

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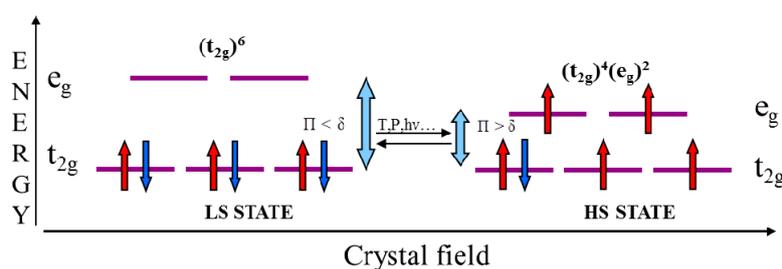
**Abstract:** There are currently extended experimental and theoretical developments of spin crossover nanomaterials, in particular based on coordination polymers for the design of smart applications. In this context, we have reproduced a three step thermal transition in a cubic spin crossover nanomaterial with a system dimension of  $5 \times 5 \times 5$  metallic centers. For this purpose, we have calculated, using Monte Carlo Entropic Sampling technique, the density of states of all possible system configurations. In order to take into account the local environment, we have included an additional interaction term in the standard Ising like model. We have then analyzed the role of this new interaction as well as the system size effect variation (from  $4 \times 4 \times 4$  to  $6 \times 6 \times 6$  metallic centers). Comparison with a 2D SCO system shows that the spin transition still proceeds in three steps but is no longer hysteretic.

**Keywords:** spin crossover; Ising model; Monte Carlo; metal organic frameworks

## 1. Introduction

The potential applications of spin crossover (SCO) materials as temperature and pressure sensors [1–3], actuators, memory devices or electrical switches [4] and their possible spin state control at the molecular level are some important assets of these fascinating switching materials. SCO coordination compounds display a central metallic ion in an octahedral environment. Considering that the central ion is an iron atom, thus, as a function of the ligand field strength, the six electron of the Fe(II) ion can occupy the 3d orbitals in two different ways giving rise to two different stable states: a diamagnetic low-spin (LS) state and a paramagnetic high-spin (HS) state (Figure 1). The transition between the two spin states can be induced by applying external perturbations such as: a temperature variation, external pressure, light irradiation, magnetic or electrical field or by a chemical adsorption-desorption phenomenon [5–10]. In the last years, several experimental studies concerning the role of cooperativity in SCO compounds have been reported [2,3,11–19] in this context giving a great attention to stepwise transitions, in particular those presenting a two-step SCO behavior. It is nowadays commonly accepted that this type of switching phenomenon results from a synergistic effect between intramolecular interactions resulting from the strong bonding between metallic centres favoring an antiferromagnetic-like state (LS-HS-LS-HS,...) and intermolecular interactions of elastic

origin favoring domains with the same spin state (ferromagnetic-like). The origin of the recently discovered three-step transitions [11–13] is however far from being understood, with little theoretical studies at present [20–25]. Indeed, various models and theoretical techniques have been developed to predict precisely the influence of perturbation factors in the evolution of thermal SCO behavior. One of the most useful theoretical tool is presumably the Ising like model which was introduced by Wajnflasz and Pick in 1971 [26]. This model was considering only the short-range interaction between switching sites. With such a limitation, this model was unable for instance to reproduce hysteretic spin transition in 1D SCO systems. Later, Bousseksou *et al.* [27] reported the modelisation of a two-step spin conversion using two “antiferromagnetically” coupled sublattices, in the mean-field approximation. Linares *et al.* [28] improved this model by introducing a long range interaction in the Hamiltonian, which they successfully applied to 1D SCO chains. Under these conditions hysteretic spin transitions or two step spin transitions were covered [29]. In 2015, Chiruta *et al.* [30] introduced a new term in the Hamiltonian, by considering a new elastic interaction between edge metallic centers with their local environment. This step allowed reproducing multi-step transitions for 1D SCO systems. In addition, Chiruta *et al.* [31] performed theoretical studies that highlighted the role of short- and long-range interactions for system metallic centers with periodic conditions. They showed that the long range interaction parameter is the basis of hysteretic spin transitions, while the short range interaction parameter is the basis of two step transitions. It was also demonstrated that the edge effect is at the origin of multi-step transitions, even if the metallic centers are fixed in the HS state [32] or are active metallic centers that interact with their local environment [30,33]. Other important theoretical results were reported considering systems architecture [34] or molecule size effects [31,35,36]. In the current account, we consider the influence of interaction between edge metallic centers with their local environment for different architectures in 2D and 3D SCO materials.



**Figure 1.** Electronic diagram of the high-spin (HS) and low-spin (LS) states for a Fe(II) ion in an octahedral ligand field.

## 2. Materials and Methods

### 2.1. Ising Like Model

To simulate the interaction between edge metallic centers with the environment, we have used the following Hamiltonian:

$$H = \frac{\Delta - k_B T \ln g}{2} \sum_{i=1}^N \sigma_i - G \sum_{i=1}^N \sigma_i \langle \sigma \rangle - J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - L \sum_{i=1}^M \sigma_i, \quad (1)$$

where  $\sigma$  is a fictitious spin operator which can take the value  $-1$  when the metallic center is in the LS state and the value  $+1$  when the metallic center is in the HS state,  $\Delta$  is the energy gap,  $k_B$  is the Boltzmann constant,  $g = g_{HS}/g_{LS}$  represents the ratio of degeneracies of the two spin states, HS and low-spin (LS),  $N$  is the number of metallic centers,  $J$  and  $G$  represent short- and long-range interactions,  $L$  is the interaction parameter of  $M$  edge metallic centers with their local environment. Since from experimental results it is clear that the environment favors the HS state, we have considered in this contribution a positive value of  $L$ .

Dimensionless macroscopic variables were also used:

$$m = \sum_{i=1}^N \sigma_i, \quad (2)$$

$$s = \sum_{\langle i,j \rangle} \sigma_i \sigma_j, \quad (3)$$

$$c = \sum_{k=1}^M \sigma'_k, \quad (4)$$

where  $\sigma'_k$  represents the metallic centers at the “surface” (edge-metallic centers).

The Hamiltonian of the system can be written:

$$H = \left( \frac{\Delta - k_B T \ln g}{2} - G \langle \sigma \rangle \right) m - Js - Lc, \quad (5)$$

The HS fraction,  $n_{HS}$ , is given by:

$$n_{HS} = \frac{\langle \sigma \rangle + 1}{2}, \quad (6)$$

where, the average fictitious magnetization can be written as:

$$\langle \sigma \rangle = \frac{\sum_{i=1, NL} \frac{m_i}{NL} d(m_i s_i c_i) \exp \left( -\frac{1}{k_B T} (-h_f m_i - J s_i - L c_i) \right)}{\sum_{i=1, NL} d(m_i s_i c_i) \exp \left( -\frac{1}{k_B T} (-h_f m_i - J s_i - L c_i) \right)}, \quad (7)$$

where  $NL$  is the number of distinct configuration of states  $\langle m, s, c \rangle$ ,  $d(m, s, c)$  is the number of configuration for a given set of values and where  $h_f$  is given by the expression:

$$h_f = - \left( \frac{\Delta - k_B T \ln g}{2} - G \langle \sigma \rangle \right), \quad (8)$$

This is a self consistent equation  $\langle \sigma \rangle = f(\langle \sigma \rangle)$  that has been solved using the bisection technique. The  $\Gamma$  interaction which has been often used by other authors in the mean field approximation [37] is equivalent to  $\Gamma = qJ + G$  where  $q$  is the nearest neighbors number.

## 2.2. Monte Carlo Entropic Sampling

We used the Monte Carlo entropic sampling (MCES) method [38] to generate a table that contains the dimensionless macroscopic variables,  $m, s, c$ , and their density,  $d(m, s, c)$ . Therefore, we used the principle of MCES described by Shteto *et al.* [39] which consists in introducing in the detailed balance equation a suited biased distribution  $P$  in order to favor configurations belonging to weakly degenerate macrostates and to dampen those belonging to the highly degenerate macrostates.

The balance equation is given by:

$$P_i W(i \rightarrow j) = P_j W(j \rightarrow i), \quad (9)$$

and the biasing probability was chosen as the inverse of the desired restricted density of states.

$$P_i \propto \frac{1}{d(m_i, s_i, c_i)}, \quad (10)$$

In this case, the balance equation can be written:

$$\frac{W(i \rightarrow j)}{W(j \rightarrow i)} = \frac{P_j}{P_i} = \frac{d(m_i, s_i, c_i)}{d(m_j, s_j, c_j)}. \quad (11)$$

Since in the first Monte Carlo step the density of the state  $d(m, s, c)$  is unknown, we put all  $d(m, s, c)$  equal to 1. So, after iteration  $k$  the density will be  $d_k(m, s, c)$ . Then, using  $d_k(m, s, c)$  as a bias, a MC sampling is run; it is termed a 'Monte Carlo stage' and yields a histogram of the frequency of the macrostates [38]:  $H_k(m, s, c)$ :

$$H_k(m, s, c) \propto d(m, s, c) \frac{1}{d_k(m, s, c)}. \quad (12)$$

The resulting restricted density of states is obtained after applying a correction for the bias:

$$d_{k+1}(m, s, c) \propto d_k(m, s, c) H_k(m, s, c). \quad (13)$$

After the table that consists from  $m, s, c$ , and  $d(m, s, c)$  is obtained, the partition function can be calculated using the following expression:

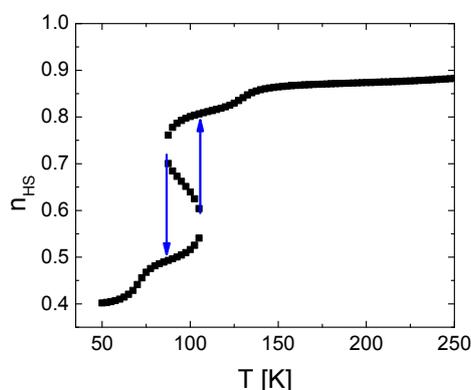
$$Z = \sum_{(m, s, c)} d(m, s, c) \exp(-\beta(-hm - Js - Lc)), \quad (14)$$

and all the thermodynamic properties of the system can then be derived analytically.

### 3. Results and Discussion

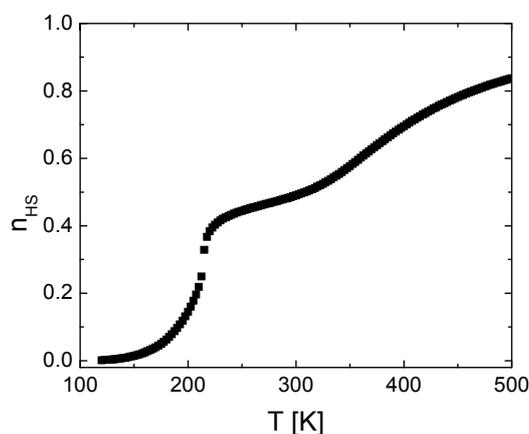
The stepwise SCO behavior observed experimentally in 3D SCO systems [11] was modelled by Chiruta *et al.* [21] considering an antiferromagnetic-like short-range interaction, a ferromagnetic-like long-range interaction and considering the system bordered with metallic centers blocked in the HS state as well. The multi-step transitions obtained experimentally for 1D and 2D SCO systems [12,13] were modelled by considering that the edge metallic centers interact with their local environment [30,33] or by blocking the edge metallic centers in HS state [31,32].

In this work, we first consider a 3D SCO system whose edge metallic centers interact with its environment and apply the bisection technique to equation (7). We derived the HS fraction,  $n_{\text{HS}}$ , from Equation (6). The SCO selected system contains 125 metallic centers ( $5 \times 5 \times 5$ ) of which 98 are surface metallic centers and only 27 are inner metallic centers. If we take into account that a typical distance between metal centers is of about 9 Å [40] it means a cubic sampling of 3.6 nm  $\times$  3.6 nm  $\times$  3.6 nm. As a result, a hysteretic multistep transition is predicted (Figure 2).



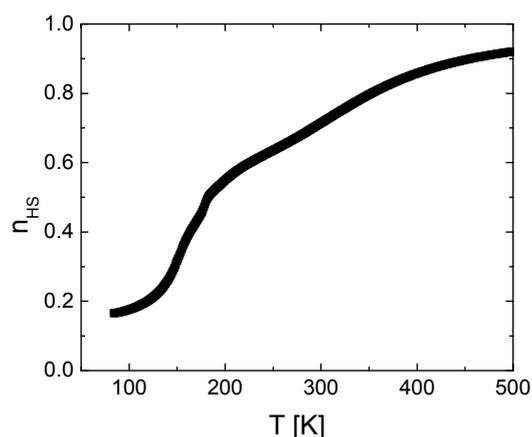
**Figure 2.** Simulated HS fraction,  $n_{\text{HS}}$ , as a function of temperature for a 3D SCO system. The computational parameters are  $N = 125$  ( $5 \times 5 \times 5$ ),  $\Delta/k_B = 1450$  K ( $=1007.75$  cm $^{-1}$ ),  $G/k_B = 470$  K ( $=326.65$  cm $^{-1}$ ),  $J/k_B = -100$  K ( $=-69.5$  cm $^{-1}$ ),  $L/k_B = 750$  K ( $=521.25$  cm $^{-1}$ ) and  $\ln(g) = 4.7$ .

For comparison purposes, we plotted the computed thermal behavior without edge effect on Figure 3. The following conclusions can be drawn: (i) the hysteresis related to the middle-step disappears; (ii) the HS fraction increases from 0 (when  $L/k_B = 0$  K) to 0.4 (when  $L/k_B = 750$  K); (iii) the transition is shifted to lower temperatures, which means that the edge interaction seems to have an action opposite to a typical applied pressure because the edge interaction favors the HS state while an applied pressure is known to favor the LS state, due to its lower ionic volume.



**Figure 3.** Simulated HS fraction,  $n_{\text{HS}}$ , as a function of temperature for a 3D spin crossover (SCO) system when  $L/k_B = 0$  K. Other parameters are the same as those of Figure 1.

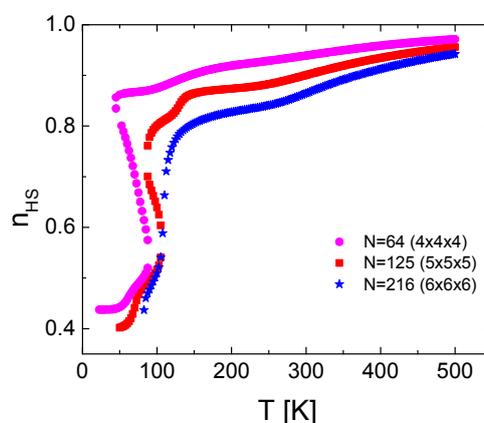
The computed thermal behavior of a 2D SCO system (where the interactions within metallic centres between planes are less than 10% of the interaction between metallic centres in the same plane) with 121 metallic centers is shown in Figure 4. Even if the number of metallic centers is almost equal to the number of metallic centers of the 3D system used above (125), the role of edge effect is reduced, because the number of edge metallic centers is only 40 compared to 98 metallic centers in the case of the 3D system. The spin transition is still incomplete, proceeds in three steps but is no longer hysteretic.



**Figure 4.** Simulated HS fraction,  $n_{\text{HS}}$ , as a function of temperature for a 2D SCO system with  $N = 121$  ( $11 \times 11$ ). Other parameters are the same as those of Figure 1.

Finally, we have investigated the increase of the system size (Figure 5). By increasing the system size, ie by decreasing the ratio between edge and inner metallic centers (from 7 for a cube system with 64 metallic centers to 3.629 for a system with 125 metallic centers and to 2.375 for a system with 216 metallic centers), the edge effect decreases and the role of inner metallic centers increases. As a

result, when we increase the size of the system, the equilibrium temperature,  $T_{1/2}$ , is shifted to higher temperatures and the transition proceeds more continuously from LS to HS.



**Figure 5.** Simulated HS fraction,  $n_{HS}$ , as a function of temperature for 3D SCO systems of different sizes. Other parameters are the same as those of Figure 1.

#### 4. Conclusions

In this communication, we have studied the role of the interaction between edge metallic centers and their local environment on the thermal behavior of spin crossover compounds. Our predictions show that: (i) it favors the high-spin state at the surface which means that it plays an equivalent role opposite to a typical applied pressure; (ii) it shifts the transition to lower temperatures and increases the residual high-spin fraction. As a result, we claim that the 3-step spin crossover originates from three interactions: (1) an interaction between edge-metallic center with the matrix; (2) a “ferromagnetic-like” long-range interaction and (3) an “antiferromagnetic-like” short-range interaction. This prediction is of the utmost importance in the current development of new spin crossover materials for smart applications.

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**Author Contributions:** J.L. proposed the subject; C.J. and J.L. performed the calculations and analyzed the data; C.J., J. L., A.R. and Y. G. wrote the paper and participated to all discussions.

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