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## Size effect on the three state thermal hysteresis of a 2D spin crossover nanoparticles

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**Abstract:** In this report first we show, in a framework of the Ising-like model, a numerical simulation of a typical two step thermal transition obtained for a square lattice 12x12: a "first-step hysteresis" for a high spin fraction  $N_{hs}$  between 0 - 0,5 and at a higher temperature a "second-step hysteresis" with  $N_{hs}$  between 0.5 and 1. As long as we decrease the number of molecules the temperature range of the "second-step hysteresis" moves to a lower temperature, until is obtained, for a square of 4x4, a clear overlapped case with a three state behaviour.

A detailed analysis on the role of the size system (4x4, 5x5, 6x6, 8x8 and 12x12) on the stability of this "Three state behaviour" is presented in this contribution. We study the influence of the surrounding environment for this specific thermal hysteresis.

To solve the self-consistent equation related to the average value of the spin-operator  $\langle\sigma\rangle$ , we use the density of the states calculated using a dynamic programming algorithm that will be presented in this paper.

### 1. Introduction

In order to find new materials that can be used for information storage, many European, Japanese and American laboratories are involved in research activities in the study of bistable molecular materials. Indeed, two- and multi-steps spin transitions are observed in these materials, a phenomenon which thus presents the advantage to open the way for three or several-bits electronics. Spin Crossover (SCO) [1-6] is one type of such compounds and particularly the SCO in six coordinate FeII complexes with two states: the diamagnetic lowspin (LS) state and the paramagnetic high-spin (HS) state. These materials can switch from one state to another by the action of external parameters (temperature,



pressure, light, magnetic fields...). Several types of transitions are depicted, including gradual and stepwise transition with two or three steps. These transitions occur at low, high or room temperature, and they even present a hysteresis effect. Ising-like model<sup>[7-11]</sup>, the atom-phonon coupling<sup>[12]</sup> or mechanoelastic models<sup>[13-14]</sup> have been proposed to explain and reproduce the switching process from LS to HS triggered by temperature, pressure, visible light or magnetic field. As a result the experimental and theoretical study, of the solid state presenting cooperative effects have become a very popular topic. Recently a new challenging problem related to the SCO nanoparticles<sup>[15-21]</sup> at nanoscale level has been highlighted, since the size of particles proved to play an important role in the cooperativity of the system, and particularly the role of edge molecules. The core/shell ratio and the interaction between edge (or surface) molecules with their surrounding are related to the hysteresis for very low numbers of molecules. In this contribution we focus on 2D SCO and we analyze the conditions to obtain a three-state behaviour. This special case is obtained for an "antiferromagnetic-like" short-range interaction together with a "ferromagnetic-like" long-range interaction and an interaction between the molecules at the surface and the surrounding matrix. We analyze the role of all these three parameters for these three-state cases. The manuscript is organized as follows: in section (2) we first present Ising-like JLG model<sup>[20,21]</sup>, with short- (J), long- (G) range interaction together with the matrix interaction (L) with the molecules at the surface that is applied in this article, then we present several results of numerical simulations conducted on the 2D lattices. The discussion of three-state behaviour obtained using several stimuli is conducted in this section. In section (3) we conclude and outline some possible extensions of the present work.

## 2. Results and discussion

### Ising Model

As a first two-states model, Wajnflasz and Pick<sup>[7]</sup> introduced the Ising model to describe the spin transition behavior in which only "short-range interaction" between the spin-crossover sites is considered, which means, for a 1D system, the four nearest neighbours. Boussekou et al.<sup>[11]</sup> made a thorough analysis of this model in the mean field approximation and they reproduce, with a negative short-range interaction, a double step spin transition. Furthermore, Linares et al.<sup>[10]</sup> introduced a long range interaction in the Hamiltonian besides the short range interaction in order to reproduce hysteresis in 2D compounds. With these contributions, the Hamiltonian include now the short and long range interactions to which we added an energetic contribution "L"<sup>[18-20]</sup>, « to the ligand-field of edge molecules of a SC nanoparticle ». This term allows us to explicitly take in account the interactions between molecules on the edge and the environment in contact, which weakens the molecules' field. In this case we can now define the Hamiltonian with the following equation:

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

This Hamiltonian makes it possible to simulate the material behaviour in an environment characterized by its interactions not only in the core of the material, but also at the edge. In the expression used for the Hamiltonian,  $\sigma$  is an operator of the fictitious spins which can take a value of -1 (the low spin state) and +1 (the high spin state),  $\Delta$  is the energy value of the gap between the low spin (LS) and the high spin (HS) states,  $g = g_{HS} / g_{LS}$  represents the ratio between the respective degeneracies,  $g_{HS}$  and  $g_{LS}$  of the HS and LS states. J and G are respectively the short and long-range interactions and L is the contribution of the interactions between the molecules on the edge (surface) and the local

environment. The addition of the constant  $L$  is based on the fact that the molecules on the surface have specific properties. Here,  $N$  is the total number of molecules in the lattice and  $M$  the number of molecules at the surface ("edge").

The following macroscopic parameters will be useful in the description of the thermodynamic properties:

$$m = \sum_{i=1}^N \sigma_i \quad s = \sum_{\langle i,j \rangle} \sigma_i \sigma_j \quad c = \sum_{k=1}^M \sigma'_k \quad (2)$$

Where  $\sigma'_k$  represents the molecules on the edge. There,  $m$  and  $c$  are the total and surface magnetizations,  $s$  is the sum of two spins correlations in the lattice.

Then the Hamiltonian can be cast as:

$$H = \left( \frac{\Delta - k_B T \ln g}{2} - G \langle \sigma \rangle \right) m - Js - Lc \quad (3)$$

We express the total number of high spins,  $N_{HS}$  or  $m'$  by:

$$N_{HS} = m' = \frac{1 + \langle \sigma \rangle}{2} \quad (4)$$

The fictitious magnetic average is given by:

$$\langle \sigma \rangle = \frac{\sum_{i=1}^{NL} \frac{m_i}{N} d(m_i s_i c_i) \exp \left( -\frac{1}{k_B T} (-h m_i - J s_i - L c_i) \right)}{\sum_{i=1}^{NL} d(m_i s_i c_i) \exp \left( -\frac{1}{k_B T} (-h m_i - J s_i - L c_i) \right)} \quad (5)$$

Where,  $NL$  is the number of possible configurations  $\{m, s, c\}$ ,  $d(m, s, c)$  is the density of states, that represents the number configuration with the same  $m$ ,  $s$  and  $c$  values and  $h$  is expressed as :

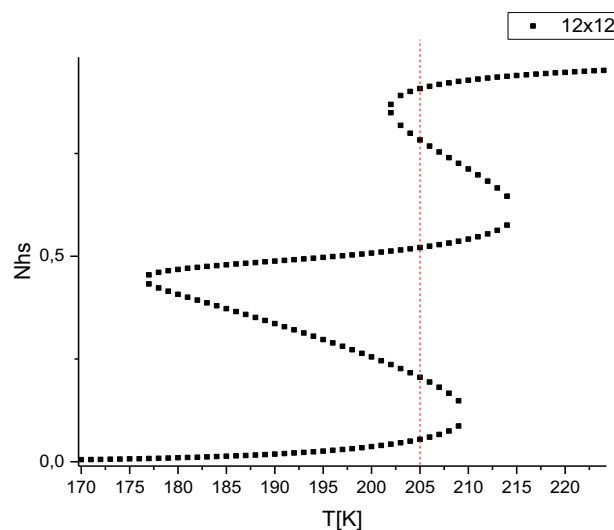
$$h = - \left( \frac{\Delta - k_B T \ln g}{2} - G \langle \sigma \rangle \right) \quad (6)$$

The density of macrostates,  $d(m, s, c)$ , and the different configurations  $\{m, s, c\}$ , have been calculated using Monte Carlo Entropic Sampling and also a new dynamic programming algorithm.

In this case we are dealing with a «self-consistent equation» ( $\langle \sigma \rangle = f(\langle \sigma \rangle)$ ) which we can solve numerically by the bisection technique.

### **Three states study**

By using the Ising-like model and the calculation technique, we study the thermal behaviour of 2D SCO nanoparticles. In order to have realistic parameters we have used in this contribution two sets of values for the degeneracy ratio  $\ln(g_{HS}/g_{LS}) = 6.01$  and the energy gap  $\Delta/k_B = 1300$  K. We performed calculations on 2D SCO with several sizes of molecules, 16, 25, 36, 64 and 144 molecules.

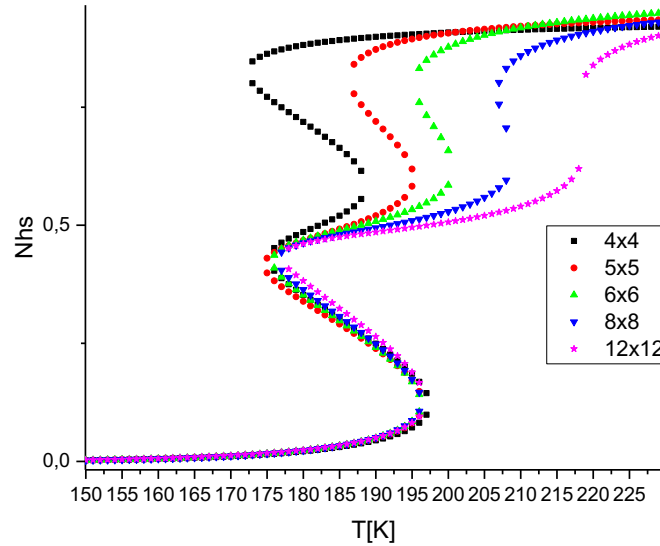


**Figure 1** Thermal behavior of the high spin fraction showing The three states hysteresis loop for 144 particles, the parameters value are  $\Delta/k_B = 1300$  K,  $G/k_B = 735$  K,  $J/k_B = -103$  K,  $L/k_B = 120$  K,  $\ln(g) = 6.01$ .

The figure 1 shows the 3 states phenomena with a 2D SCO compounds, these three states are represented in two hysteresis loops, the first step hysteresis between 175 – 210 K and for  $n_{HS}$  between 0 – 0.5, and the second one between 203 – 215 K with  $n_{HS}$  between 0.5 – 1. The branch between 0-0.5 in the Figure 1, as well as that one between 0.5-1 are the unstable states and so are not observed experimentally. The plateau that is obtained between 175 – 215 K for  $n_{HS}$  around 0.5 is constructed by sequence of +1 and – 1 and is due to the strong negative value of the short-range  $J$ . The two hysteretic loops that overlap lead to a three stable states behaviour for intermediate temperatures. For  $T = 205$  K three states are obtained respectively for values of  $n_{HS}$  around 0, 0.5 and 1 between  $T_1 = 290$  K, and  $T_2 = 303$  K these states seem to be stable. These states can be achieved by proper variation of temperatures and other physical stimuli such as light.

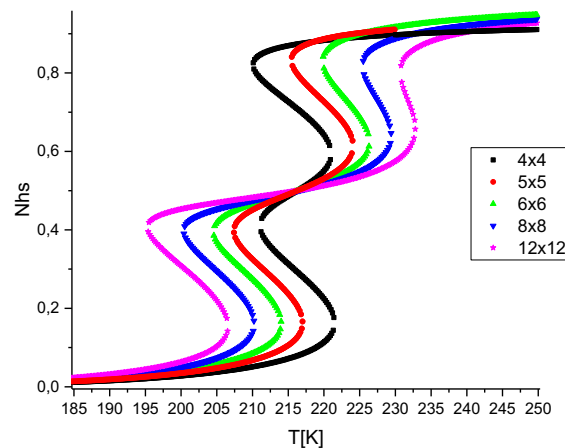
### **a. Size effect**

Using  $J/k_B = -103$  K,  $G/k_B = 655$  K and  $L/k_B = 120$  K our numerical calculations show that with a size of  $N = 16$  a two hysteresis loop for an interval ( $\Delta T = T_2 - T_1 = 13.36$  K) is obtained (Figure 2). Increasing the size will reduce the hysteresis loop width  $\Delta T$  until it is completely lost from size  $N = 64$ . We observe that the evolution of the loop width  $\Delta T$  vs. size  $N$  is quite linear and the second step hysteresis disappear gradually for high sizes, which means that above certain size we will obtain one hysteresis step.



**Figure 2** Thermal evolution of the hysteresis loop for different sizes: 4x4(black square), 5x5(red circle), 6x6(green up triangle), 8x8(blue down triangle), 12x12(purple star), the parameters' value are  $\Delta/k_B = 1300$  K,  $G/k_B = 655$  K,  $J/k_B = -103$  K,  $L/k_B = 120$  K,  $\ln(g) = 6.01$ .

For a value of  $L/k_B = 0$  K, we see the same behavior of the two hysteresis loops, but the transition remain constant at the value of  $T_{eq} = \frac{\Delta}{\ln(g)}$ . (Figure 3).

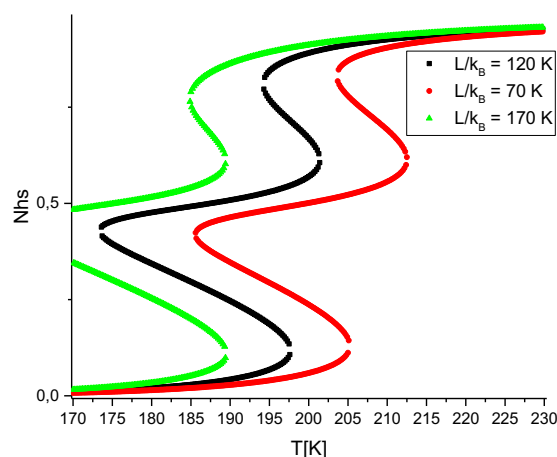


**Figure 3** Thermal evolution of the hysteresis loop for different sizes: 4x4(black square), 5x5(red circle), 6x6(green up triangle), 8x8(blue down triangle), 12x12(purple star), the parameters' value are  $\Delta/k_B = 1300$  K,  $G/k_B = 655$  K,  $J/k_B = -103$  K,  $L/k_B = 0$  K,  $\ln(g) = 6.01$ .

### **b. The role of matrix interaction L**

The role of the matrix interaction with the environment ( $L$ ) on the thermal behavior is presented in Figures 4. For a relatively low value of environment interaction we have the first and second step

hysteresis separated. Each hysteresis has its own temperature interval, for a value of  $L/k_B = 120$  K we obtain a coexistence of the first and second step hysteresis with practically the same Temperature interval; for a high value of  $L$  we can also have the coexistence with a double step upon heating but we lose the second step hysteresis width and the first one become bigger.



**Figure 4** Evolution of molecules in the HS state  $N_{hs}$  as a function of temperature, for a 2D system  $N=36$  molecules, for different matrix interactions strength:  $L/k_B=70$ K (Red circles);  $L/k_B=120$ K (Black squares);  $L/k_B=170$ K (green triangles). The parameter values are  $\Delta/k_B = 1300$ K,  $\ln(g)=6.01$ ,  $G/k_B = 675$  K,  $J/k_B = -103$  K.

### 3. Conclusions

In the framework of the Ising-like, the JLG extension<sup>[18-20]</sup> takes into account the short-, long-range interaction as well as the interaction between molecules at the surface with the environment. From its application, we have showed that this last interaction, can control the three states behaviour in a 2D SCO compound as well as the hysteresis loop temperature interval. We have also analyzed the role of the number of molecules (size) in the stability of this three-states case. It is firmly expected that this particular case can be proposed for a three states electronic storage system.

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