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# Matrix and size effects on the appearance of the thermal hysteresis in 2D spin crossover nanoparticles.

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## Abstract

The Ising-like model is used to simulate the thermal behavior of a 2D spin crossover (SC) nanoparticle embedded in a matrix, which affects the ligand field at its surface. First, we discuss the standard case of the isolated nanoparticle, and in the second part we consider the effect of the interaction between edge molecules and their local environment. We found that in the case of an isolated SC nanoparticle presenting a gradual spin transition, the matrix effect may drive a first-order spin transition accompanied with a hysteresis loop. An in-depth analysis of the physical mechanism underlying this unusual property is performed, leading to build up the system's phase diagram which clarifies the conditions of appearance of the first-order transition in the current 2D SC nanoparticles as function of their size and the strength of their interaction with their immediate environment.

Keywords: Spin croosver  
nanoparticles  
phase transition  
Ising model

## I-Introduction

SC compounds are molecular materials containing metal ions with the  $3d^4-d^7$  electronic configuration in octahedral symmetry [1]. The most studied SC compounds are Fe(II)-based materials, where Fe(II) is coordinated to Nitrogen atoms. In such configuration, Fe(II) may present two different spin states, namely low-spin (LS) and high-spin (HS), inter-switchable by several external stimuli, like temperature, pressure, light irradiation or magnetic field [2-10]. The

diamagnetic LS state (of electronic configuration  $t_{2g}^6 e_g^0$  for Fe-II) has a minimum total spin  $S=0$ , while the paramagnetic HS state (of electronic configuration  $t_{2g}^4 e_g^2$  for Fe-II) displays a maximum total spin,  $S=2$ . In addition to the spin state changes, the spin transition is accompanied by a variation in the color, the volume (which usually increases by at least 3%) and electric conductivity [11-13] of the materials. Due to their potentialities in several types of applications, related to information storage or actuation, extensive experimental and theoretical research efforts of the last years were dedicated to explain how the interactions between molecules influence the properties of SC solids. Among these works, the main theoretical models were based on the use of atom phonon coupling [14-17], Ising like [18,19,20] or mechano- and electro-elastic [21-22] descriptions, in combination with experimental investigations of first order reversal curves (FORC) [23-25] and optical microscopy visualizations [26,27]. In all these studies, the research of the control of the thermal hysteresis loop, and particularly, the identification of the relevant physical parameters allowing monitoring the hysteresis width is a key point for the practical applications of these systems.

The current work aims to address this problem on SC nanoparticles on which an extensive work was devoted this last decade, both from the chemical view point by synthesizing new core-shell systems [28-30] and from the theoretical side, in which some attempts to explain the interplay between the matrix and the SCO properties [31-36] have been developed. Mikolasek et al [37] has studied the influence of surface/interface on the lattice dynamic of SCO nanoparticles using a spring-ball model.

Indeed, the last years many experimental studies concerned the effect of the system size on the behavior of SC nanoparticle [37-41]. In this context, different values were reported for the critical size, under which a SCO transition loses the first-order character and exhibits a gradual conversion without hysteresis. In their study, Rotaru et al. [24] for example, have reported a critical size of about 45-50nm for the  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{Br})_2 \cdot 3\text{H}_2\text{O}$  ( $\text{NH}_2\text{trz}$  = 4-amino-1,2,4-triazole) SCO system, while Forestier et al. [42] have found a critical size value of ~30nm. Much more smaller sizes of about ~5nm [43] were also reported, reviving the debate, and making theoretical studies, to clarify the situation, highly desired. Recently Peng and al. [44] have shown experimentally, using magnetic investigations, the existence of a re-entrance behaviour on small (few nanometer size-scale) spin-crossover particles: when decreasing the size from 110nm to 12 nm the hysteresis's width reduces until it disappears completely (the spin transition becomes gradual) and they observed a recurrence of the hysteresis for particles of 2 nm size.

Here, we consider this problem in the frame of the Ising-like a model in which we include the effect of the environment on the SC nanoparticles and we study its impact on the macroscopic thermal properties of the system. The manuscript is organized as follows: Sec. II presents the model, the results and the discussion of our investigations, and in Sec. III, we conclude.

## II-Model and Results

Wajnflasz and Pick [18] have first introduced the Ising-like model to describe the spin transition phenomenon by taking into account only short-range interactions between the spin-crossover sites. Later on, Bousseksou et al. [19] have simplified this model by using only two states instead

of the fourth states suggested by Wajnflasz and Pick [18], and adapted it to describe the two-steps spin transitions in the frame of the mean field approximation. In order to reproduce hysteresis in 1D compounds Linares et al. [20] have introduced, besides the short range interaction, also a long range one in the Hamiltonian. In the present contribution, the Hamiltonian includes short- and long-range interactions, to which we have added an energetic contribution,  $L$ , to the ligand-field of edge molecules of a SC nanoparticle. This term takes into account for the interaction between surface molecules and their local environment, which results in a weakening of their ligand field. In this context, the total Hamiltonian can be written as follows:

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

where,  $\Delta$  is the energy gap between LS and HS states,  $g = g_{HS}/g_{LS}$  represent the ratio between the respective degeneracies,  $g_{HS}$  and  $g_{LS}$  of the HS and LS states.  $J$  and  $G$  are the short and long-range interactions between the SC units which are represented here by fictitious spins  $\sigma_i$  having two eigenvalues  $+1$  and  $-1$ , respectively associated with the HS and the LS states.  $L$  is the additional contribution to the ligand-field restricted only to molecules located at the edge of the nanoparticle. Indeed, molecules situated at the surface of the nanoparticle can be considered as being at the interface between the nanoparticle and its immediate environment (matrix, air, ...) and therefore, it is legitimate to consider that they have specific properties. Figure 1 illustrates the thermal-dependence of the HS fraction for an isolated SC nanoparticle having a homogeneous and constant ligand field on all sites including those located at the surface. Obviously, this situation corresponds to the case where  $L = 0$  in Hamiltonian (1).

Hamiltonian (1) was exactly solved in the canonical approach, using parameter values chosen from typical data in spin-crossover literature, such as,  $\Delta/k_B = 840\text{K}$ ,  $J/k_B = 10\text{K}$ ,  $G/k_B = 115\text{K}$ ,  $\ln(g) = 6.9$  (leading to a molar entropy change  $\Delta S \approx 56\text{J.K}^{-1}.\text{mol}^{-1}$ ), except for  $L$  which is a variable parameter.

This study is carried out for several lattice sizes, containing a number  $N = N_x \times N_y$  of molecules. The results of Fig. 1 show that, in all cases, a first-order transition is observed whose thermal hysteresis loop increases with the lattice size. As it was expected, the equilibrium temperature  $T_{1/2} = \frac{\Delta}{k_B \ln g} = 121.7\text{K}$  remains size-independent.

Fig 2a displays the associated phase diagram  $\Delta/k_B$  as function of  $T$  for two values of size,  $N=30$  ( $5 \times 6$ ) and  $N=16$  ( $4 \times 4$ ). Let's consider the case  $N=30$ . For a compound with  $\Delta/k_B$  higher than the critical ligand field value,  $\Delta_C/k_B = 997\text{K}$ , the spin transition from LS to HS occurs gradually, i.e. without thermal hysteresis. It is worth to notice that if for some reason (like, the interaction of the SC nanoparticle with some surrounding shell) the average value of  $\Delta/k_B$  decreases to the extent that  $\Delta/k_B$  becomes smaller than the critical value  $\Delta_C/k_B$ , which drives the appearance of the thermal hysteresis.

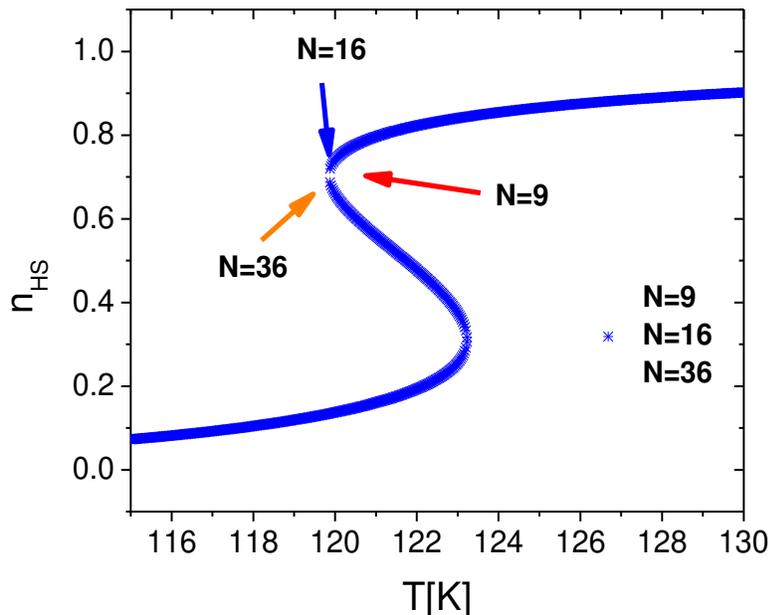


Figure 1. Simulated thermal dependence of the HS fraction for 2D SCO system for three numbers of molecules, showing the dependence of the thermal hysteresis on size. Parameters values, used in calculations, are:  $\Delta/k_B=840\text{K}$ ,  $J/k_B=10\text{K}$ ,  $G/k_B=115\text{K}$ ,  $L/k_B=0\text{K}$ ,  $\ln(g)=6.9$ .

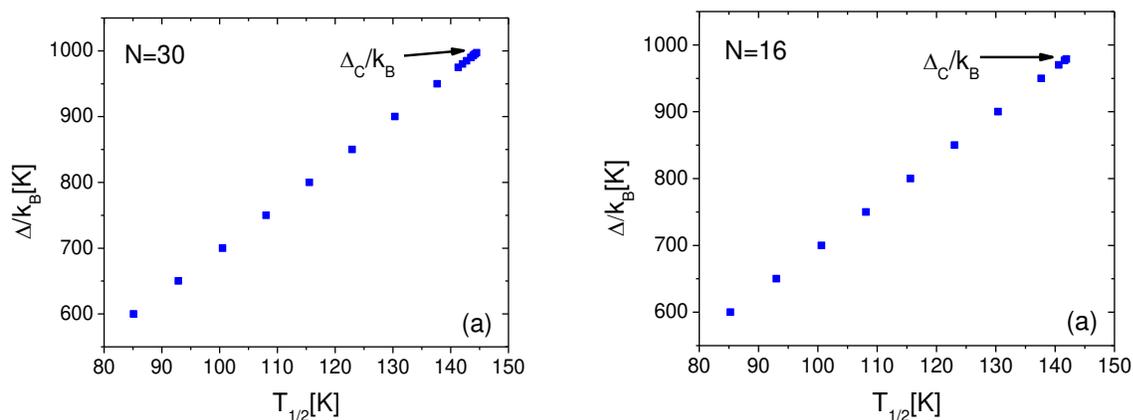


Figure 2. Phase diagram in  $T_{1/2}$ - $\Delta$  coordinates for an isolated SC nanoparticle of size (a)  $N=30$  and (b)  $N=16$ , leading to the respective critical ligand field values  $\Delta_C/k_B=997\text{K}$  and  $979\text{K}$ . The parameter values are the same as those of Fig. 1.

We have made extensive simulations of thermal dependences of the HS fraction for different ligand field values and various nanoparticle sizes. For each size, we determined the critical ligand field above which the first-order spin transition vanishes. The results are summarized in Fig. 3, where we represent the size dependence of these critical  $\Delta/k_B$ -values. It is important to

notice that the critical value of energy gap increases with  $N$  till saturation, which occurs for  $\Delta_C/k_B \sim 1000\text{K}$ , corresponding more or less to  $\Delta_C/k_B$  value at the thermodynamic limit.

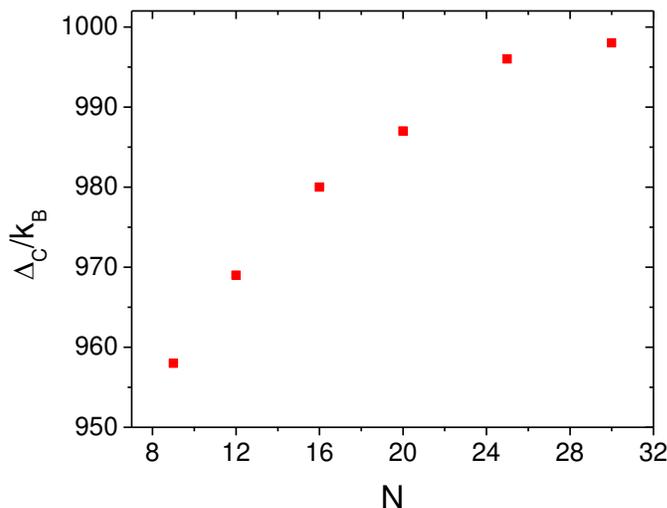


Figure 3. Size-dependence of the critical ligand field showing a monotonous increase and a saturation announcing the proximity of the thermodynamic limit. The parameter values are the same as those of Fig. 1.

In the second part of this manuscript, we explore the problem of a 2D SC nanoparticle under the influence of a matrix or a shell. In this case, the parameter  $L$  in Eq. (1), accounting for the existence of a specific ligand field of the edge atoms, enters to play. The thermal behavior of a 2D SC system including surface effects is reported in Fig. 4, for various value of the system size. We observe that, contrary to the case of an isolated nanoparticle (see Fig. 1), now the transition temperature  $T_{1/2}$  shifts to higher temperatures with the nanoparticle size, while concomitantly the width of the thermal hysteresis shows a very unusual trend, since it increases when decreasing the nanoparticle size. One of the important conclusions arising from these results is the emergence of the first-order transition at small sizes, while it was absent at bigger sizes, as a result of surface effects, which then constitute a surface-driven first-order transition. This result is very original, and to our best knowledge it was never reported in the theoretical literature. The phase diagram giving the size-dependence of the critical ligand-field,  $\Delta_C/k_B(N)$ , is presented in Fig. 5. Now,  $\Delta_C/k_B(N)$  is an increasing function of the size, a behavior which clearly contrasts with the case of the isolated nanoparticle, given in Fig. 3.

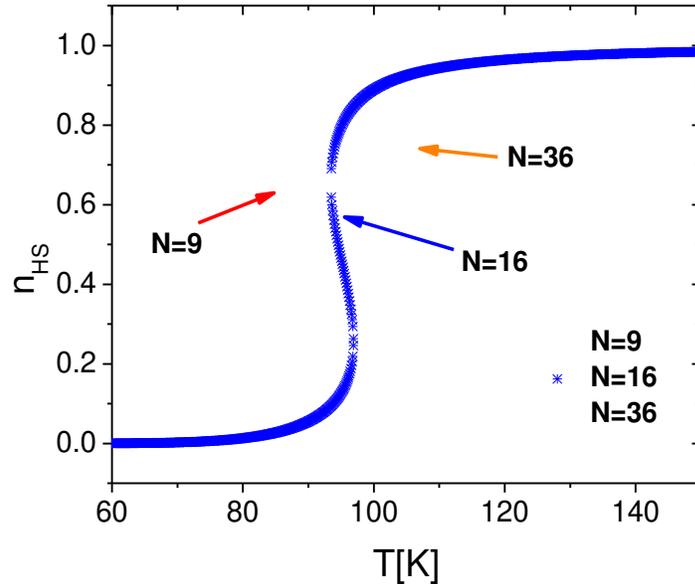


Figure 4. Simulated thermal dependence of the HS fraction for 2D SCO nanoparticle including surface effects, for three numbers of molecules. Remark the behavior of the thermal hysteresis width and equilibrium temperature with size. The parameter values are the same as those of Fig. 1, except for  $L/k_B=120\text{K}$ .

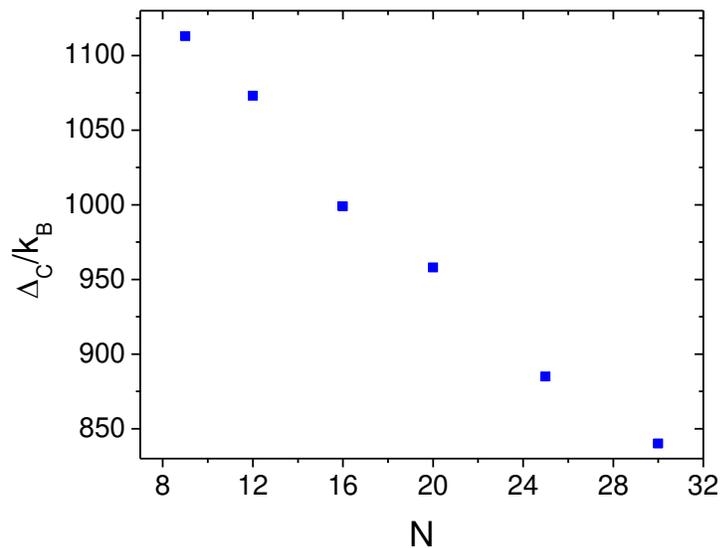


Figure 5. Size-dependence of the critical value of the energy gap as function of the number of molecules for a 2D SC system embedded into a matrix. The computation parameters were the same as those of Fig. 4.

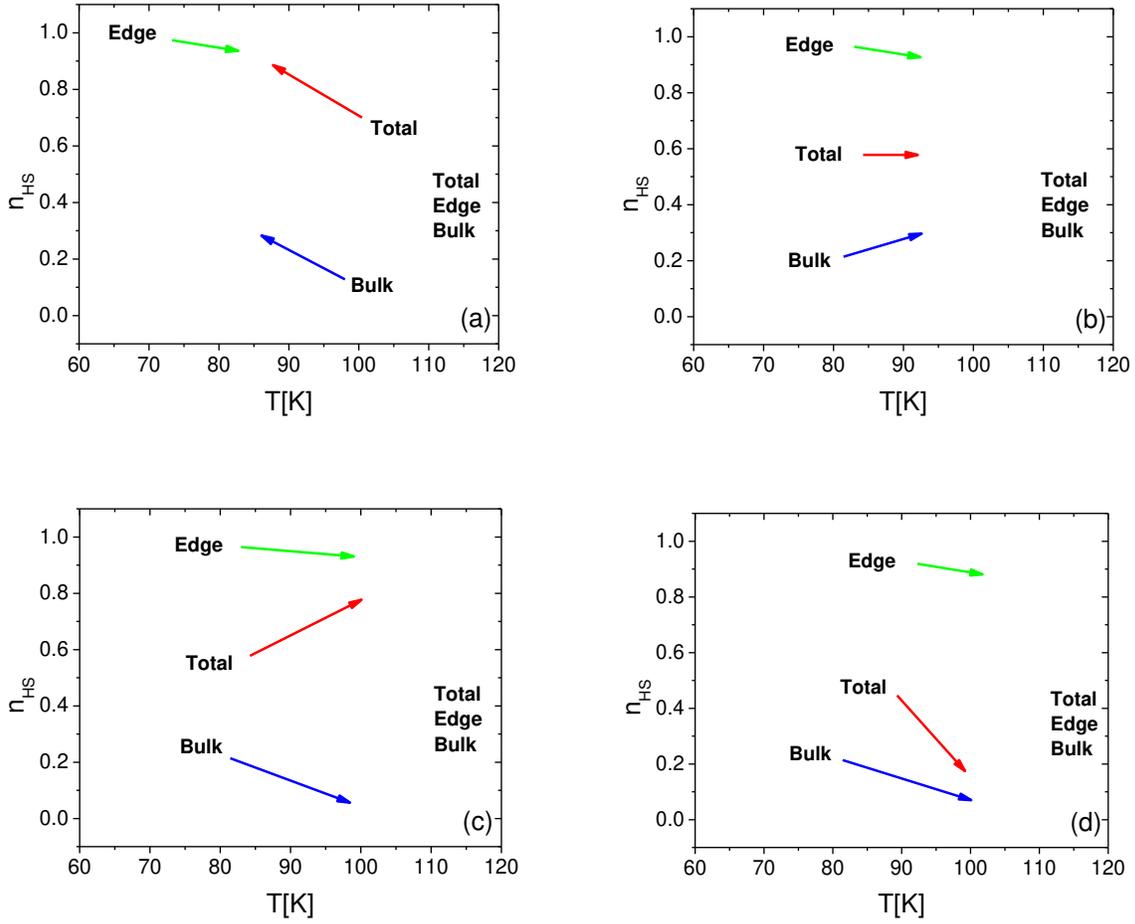


Figure 6. Thermal evolution of the high spin molar fraction,  $n_{\text{HS}}$ , for a 2D system embedded into a matrix for the sizes: (a)  $N=9$  ( $3 \times 3$ ), (b)  $N=16$  ( $4 \times 4$ ), (c)  $N=25$  ( $5 \times 5$ ) and (d)  $N=36$  ( $6 \times 6$ ). The parameter values are:  $\Delta/k_B=840\text{K}$ ,  $J/k_B=10\text{K}$ ,  $G/k_B=115\text{K}$ ,  $L/k_B=120\text{K}$  and  $\ln(g)=6.9$ .

To disentangle the surface and the bulk contributions in the thermal dependence of the total HS fraction of Fig. 4, we have calculated the thermal evolution of the HS fraction corresponding to each of them, for various sizes, that we illustrate in Fig. 6. It clearly appears in this figure that the thermal dependence of the surface (green curve) and bulk (blue curve) contributions are dramatically influenced by the ratio of the numbers of edge/bulk (surface/volume in 3D) molecules. Thus, for the first case (figure 6a) whose ratio 8:1 states that the surface is dominant, the thermal behavior of the system is mainly governed by that of the edge molecule, whose expected transition temperature  $T_{1/2}(\text{surface}) = \frac{\Delta - 2L}{k_B \ln g} \approx 87\text{K}$  is (significantly different from that of the bulk system, given by  $T_{1/2}(\text{bulk}) = \frac{\Delta}{k_B \ln g} \approx 121.7\text{K}$ ) is in excellent agreement with the simulation. The influence of edge molecules on the global behavior of the system (red curve), weakens with increasing the system size, which is confirmed by the shift of the transition temperature towards that of the bulk material. Despite of these simple considerations, the thermal

behavior of the bulk and the edge HS fractions are quite complex (see the shapes of the blue curves), due to their interplay and a complete description will be developed elsewhere.

### III-Conclusion

Among the principal effects of the interaction between the matrix and the edges (or surfaces) molecules, reported in this work, the reduction of the energy gap between LS and HS states of surface atoms. For some particular cases, in 2D SC nanoparticles, may deeply affect the thermal transition and lead to a qualitatively different thermal behavior than usual expectations. We demonstrated that specific weaker ligand field at the surface of SC nanoparticles may lead to the emergence of a thermal hysteresis (i.e., a bistability) at small sizes even if the latter was absent for bigger sizes. This results can be related to the experimental data recently obtained by Peng et al. [44] and it revives the debate about the existence or not of a thermal bistability (i.e. thermal hysteresis) in SC nanoparticles. This point is of higher importance for potential application of SC nanoparticles as rapid switching devices, since the existence of a bistability is necessary at this scale. One should however underline the important effect of the long-range interactions in the present study, which was considered as insensitive to the system size and which probably merits a careful examination and developments in further works.

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