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Monte Carlo - Metropolis Investigations of Shape and Matrix Effects in 2D and 3D Spin-Crossover Nanoparticles

Salim Guerroudj[1,2], Rafael Caballero[3], Francisco De Zela[3], Catalin Jureschi[2,4], Jorge Linares[5*], Kamel Boukheddaden[5*]

[1] Département de Sciences Physique, UVSQ, Université Paris Saclay, F-78035 Versailles Cedex, France.
[2] LISV, Université de Versailles Saint-Quentin-en-Yvelines, Université Paris Saclay, Velizy 78140, France
[3] Departamento de Ciencias, Sección Física, , Pontificia Universidad Católica del Perú, Apartado 1761 - Lima, Peru
[4] Faculty of Electrical Engineering and Computer Science & Research Center MANSiD, Stefan cel Mare University, Suceava 720229, Romania; catalin.jureschi@gmail.com
[5] GEMaC, Université de Versailles Saint-Quentin-en-Yvelines, CNRS-UVSQ (UMR 8635), Université Paris Saclay, Versailles Cedex 78035, France

E-mail**:** jorge.linares@uvsq.fr, Kamel.bouheddaden@uvsq.fr

Abstract. The Ising like model, taking into account short- , long-range interaction as well as surface effects is used to investigate size and shape effects on the thermal behaviour of 2D and 3D spin crossover (SCO) nanoparticles embedded in a matrix. We analyze the role of the parameter *t*, representing the ratio between the number of surface and volume molecules, on the unusual thermal hysteresis behaviour (appearance of the hysteresis and a re-entrance phase transition) at small scales.

1. Introduction

There has been a growing interest, in recent years, in the design of SCO nanoparticles [1-6] with controlled shape and environment, due to their serious potential applications as sensors, switchable and reversible memories or nano-actuators. The Fe-II based SCO solids are able to switch thermally (but also under several other external stimuli such us: light, pressure, magnetic field etc.) between two spin states, namely the paramagnetic high spin (HS) and diamagnetic low-spin (LS) states, characterized by the associated respective spin values S=2 and S=0. The experimental studies confirmed the role of the surface effects leading to unusual and non-trivial size dependence of their bistable character. In particular in some cases, the SCO nanoparticles may show a cooperative switching accompanied with a thermal hysteresis at small sizes while they exhibit gradual conversions (no phase transitions) at bigger sizes, which goes

against common sense of usual thermodynamics. Even thought, in some special cases, re-entrant phase transitions are obtained with size. The physical mechanisms at the origin of these intriguing behaviours remain however still misunderstood and so their modelling becomes mandatory. In this contribution, we investigate the above cited effects on SCO materials, by means of an Ising-like Hamiltonian [7-11] including short and long-range interactions as well as the interaction of the edge molecules of the system with their local environment. The Hamiltonian is solved in the frame of Monte Carlo Metropolis (MCM) procedure for 2D ($N_x \times N_y$) rectangular-shaped and 3D parallelepiped ($N_x \times N_y \times N_z$) SCO nanoparticles. The thermal dependence of the high-spin fraction is then derived for different particle sizes and the results are discussed with the help of analytical predictions allowing to evaluate the size dependence of the transition temperature and the conditions of occurrence of the re-entrant phase transition. In practice, the latter emerged from the Monte Carlo (MC) simulations below some critical nanoparticle size and for well identified conditions on the model parameter values.

2. The model

Based on the previous theoretical investigations of Linares and co-workers [5, 11] accounting for the matrix effect in a spin-crossover system including short and long range interactions, the Hamiltonian of the SCO nanoparticle writes:

$$H = \frac{\Delta - k_B T \ln g}{2} \sum_{i=1}^{N_t} \sigma_i - J \sum_{<i,j>} \sigma_i \sigma_j - G < \sigma > \sum_{i=1}^{N_t} \sigma_i - L \sum_{i=1}^{N_s} \sigma_i \,, \tag{1}$$

In (1), Δ is the energy difference E(HS) ─ E(LS) between the spin states of isolated molecules, G is the long-range part of the interaction, which is identified as due to lattice phonons and volume change accompanying the spin transition, J is a coupling parameter accounting for short-range ferroelastic interactions between spin states, here limited to first-neighbouring molecules. The last energetic contribution L (>0), limited to surface atoms (their number is equal to N_s), describes the additional "negative" ligand-field felt by the surface atoms.

The HS and LS states are associated with the +1 and -1 values of the fictitious spin operator, σ, with their respective different degeneracies $g+$ and $g-$, the ratio of which, is denoted, $g = \frac{g+}{g-}$. These degeneracies account for both internal (spin, orbit and intermolecular vibrations) and external (lattice phonons) degrees of freedom.

In order to simplify the expression of the Hamiltonian (1), we introduce dimensionless macroscopic variables, m, s and c, given by:

$$m = \sum_{i=1}^{N_t} \sigma_i \,, \tag{2}$$

$$s = \sum_{<i,j>} \sigma_i \sigma_j \tag{3}$$

$$and\ c = \sum_{i=1}^{N_s} \sigma_i \tag{4}$$

which are respectively associated with the total fictitious magnetization, two spin correlations and, the surface fictitious magnetization. Within these parameters, the total Hamiltonian (1) re-writes as:

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

The associated bulk and surface order parameters of the system, denoted here m_V and m_s are then simply defined as:

$$m_V = \langle \sigma_V \rangle = \frac{\sum_{i=1}^{N_t} \sigma_i}{N_t}, \tag{6}$$

$$\text{and } m_s = \langle \sigma_s \rangle = \frac{\sum_{i=1}^{N_s} \sigma_i}{N_t} \tag{7}$$

For a 2D square-shaped lattice, the quantity, $N_t = N_x^2$, is the total number of atoms, which can be expressed as the sum of the number of atoms in the bulk (core) $N_c = (N_x - 2)^2$ and those in the edge $N_s = 4(N_x - 1)$. Table 1 summarizes the values of the parameters N_t, N_c and N_s for a square lattice and for a rectangular one.

Table 1. Number of atoms for different lattice.

	Total	**Edges**	**Core**
Square Lattice	N_x^2	$4(N_x-1)$	$(N_x-2)^2$
Rectangular Lattice	$N_x N_y$	$2(N_x+N_y-2)$	$(N_x-2)(N_y-2)$

For the sake of precision, two methods have been used depending on the sample's size and the geometry dimension. For small (resp. large) samples, namely for N_t < 144 (resp. N_t > 144) atoms, we solved the Hamiltonian (1) exactly by using the entropic sampling method (resp. MC simulations) already introduced in the previous papers [5, 11].

3. Results and discussions

First, we consider a 2D SCO system, in which we look for the size-dependence of the re-entrance phenomenon and in a second stage; we study the shape effect, on the thermal properties of a SCO nanoparticle, at fixed number of molecules.

3.1. 2D Size Effects

For small samples, we solved exactly Hamiltonian (1) in the canonical approach using the entropic sampling method, in order to investigate the size-dependence of the thermal hysteresis of the high-spin fraction, n_{HS}, defined as $n_{HS} = \frac{1+m}{2}$ where m is the net fictitious magnetization per site. The results of the simulations are summarized in the figures 1 and 2, corresponding to the respective lattice sizes 3 x 3 and 5 x 5. Used parameters were: Δ/k_B = 840 K, G/k_B = 115 K, L/k_B = 120 K, J/k_B = 15 K and ln(g) = 6.9. If we take into account that a typical distance between metal centers is of about 9 Å [12] a lattice size of 3 x 3 is equivalent to a square nanoparticle of 2.7 nm x 2.7 nm

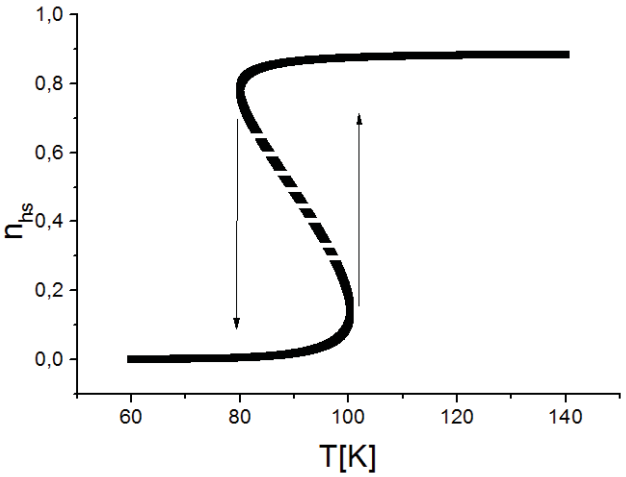

Figure 1. Exact thermal dependence of the HS fraction for a SCO nanoparticle of 9 (3 x 3) molecules, equivalent to ~3.25 nm^2 size.

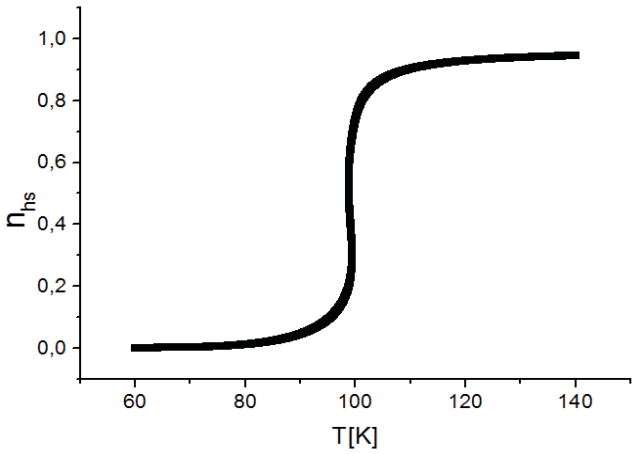

Figure 2. Exact thermal dependence of the HS fraction for a SCO nanoparticle of 25 (5 x 5) molecules, equivalent to ~ 13 nm^2 size.

As we can see in Figs. 1 and 2, the width of the thermal hysteresis decreases as the nanoparticle size increases, as a result of surface active molecules. Concomitantly, the transition temperature is lowered from ~100 K to 90 K when the size of the nanoparticle decreases from 5×5 to 3×3, respectively. The last temperature is indeed very close to the expected transition temperature of the surface atoms, evaluated to be $\frac{\Delta - 2L}{k_B \ln g} \approx 87K$, which in excellent agreement with the simulation results. In the case of 3×3 molecules, 90% of the molecules are situated at the surface (here on the edges of the lattice), and therefore the surface effect exceeds that of the core, leading to the first-order transition of Fig. 1. In this case, the SCO transition takes place at the surface of the nanoparticle and drives that of the core. In the second case of Fig. 2, corresponding to a nanoparticle of 5×5 size, the thermal hysteresis vanishes, and the system exhibits a gradual spin transition between the LS and the HS states. In this case, more than 1/3 of the SCO molecules are located in the core of the nanoparticle, so their contribution is significant and competes with that of the edge atoms.

The exact resolution based on the entropic sampling method has serious limitations when increasing the lattice's size, as for most of the exact calculations at dimensions higher that one. Therefore, Monte Carlo (MC) simulations are used to investigate bigger samples in which we kept the same parameter values as previous exact calculations. Here, we use a MC resolution, based on Metropolis transition rates. The temperature is changed with 0.5 K step, and at each temperature 1000 MC steps are used to reach the thermal equilibrium, followed by 100 MC steps, along which we perform all the statistics. The results of the simulations are displayed in Figs. 3 and 4 for the respective lattice sizes 20×20 and 25×25. Thus a gradual spin transition is obtained until we reach a threshold size at which the thermal hysteresis reappears, indicating the presence of a re-entrance phenomenon.

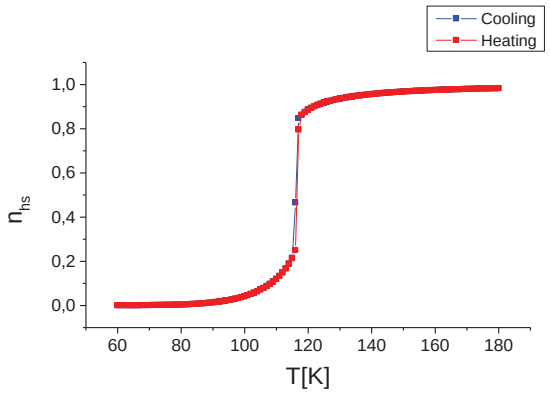

Figure 3: Simulated HS fraction for a SCO nanoparticle of 400 (20x20) molecules, equivalent to a square platelet of ~292 nm^2 size.

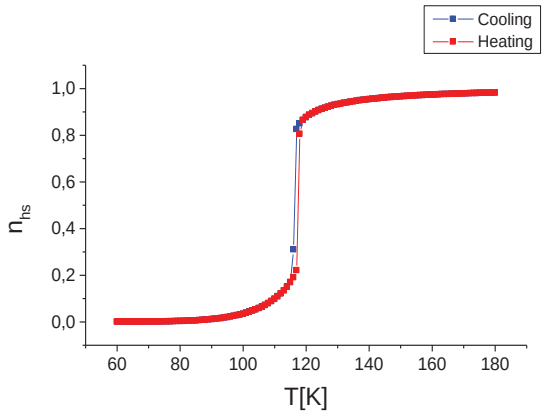

Figure 4: Simulated HS fraction for a SCO nanoparticle of 625 (25x25) molecules, equivalent to square platelet of ~ 466 nm^2 size.

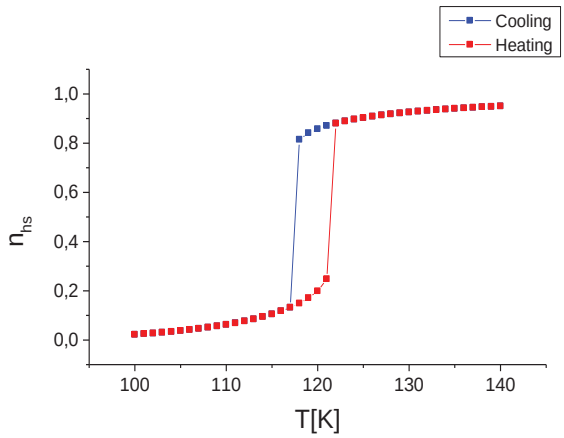

Figure 5: Simulated HS fraction for a SCO nanoparticle of 2500 (50x50) molecules configuration, equivalent to a square platelet of ~1945 nm² size.

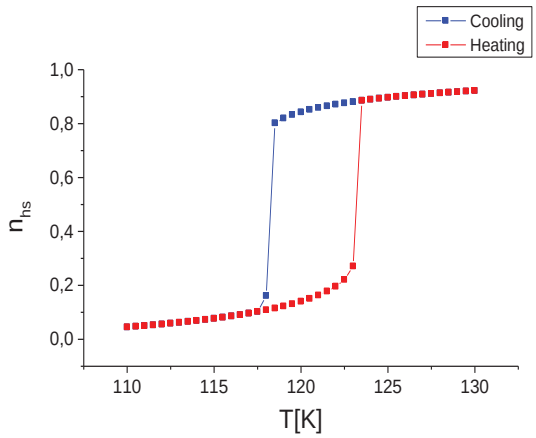

Figure 6: Simulated HS fraction for a SCO nanoparticle of 14400 (120x120) molecules configuration, equivalent to square platelet of ~ 11470 nm² sizes.

As shown in Fig. 3, for the case of 400 molecules does not lead to a thermal hysteresis for the present temperature kinetics used in the simulations: 1000 MC steps are used to reach the thermal equilibrium, followed by 100 MC steps. Here the ratio between the number of surface and bulk atoms is equal to ~11%, which remains quite small to drive a spin transition at the surface. On the other hand the transition temperature at the surface is located around 90 K, while that of the infinite system (in which the surface effects are negligible) is given by $\frac{\Delta}{k_B \ln g} \approx 122\,K$, a results which matches very well the results of Figs. 5 and 6. The case of 20×20 size is interesting, because it leads to realize the existence of a threshold size in

the existence of a bistability for the bulk atoms. This is due to short range contribution whose effect depends on the size [13]. The thermal hysteresis appears clearly at bigger size as shown in figures 5 and 6, the transition from LS to HS of the surface and bulk atoms takes place at two well separated temperatures (90 K and 120 K), with a negligible contribution of the of the edge molecules due to their weak number compared to that of bulk atoms.

3.2. 2D Shape Effects

This section is devoted to the analysis of the shape effect in SCO nanoparticles. Indeed, the ratio surface/volume atom in a nanoparticle strongly depends on the shape of the nano-object. Here, we consider a nanoparticle containing a fixed number (let's say 36) of SCO molecules and we analyse all possibilities of shape constructions for square- and rectangular-shaped lattice configurations. We associate to each of them the parameter *t*, which represents the ratio between surface and volume numbers of molecules. Thus, for a square 6 x 6, we obtain $t = 0.56$, while for rectangular-shaped SCO nanoparticles of size, 9 x 4, 12 x 3 and 18 x 2, the respective *t* values are 0.61, 0.72 and 1. As shown in Fig 7a, the increase of t value drives the appearance of a first-order transition accompanied with a hysteresis loop, the width of which increases with *t*. Interestingly, we found that the transition temperature (that is approximately the centre of the hysteresis) follows a decreasing linear plot (see Fig. 7b) with the ratio *t*, which demonstrates that surface atoms are at the origin of this behaviour.

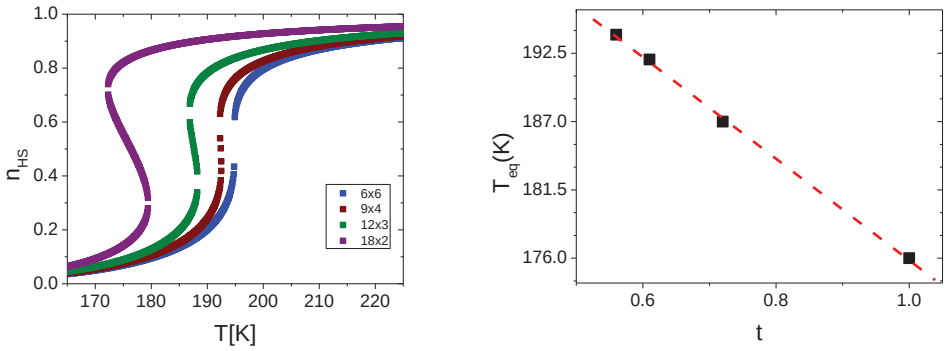

Figure 7. (a) The simulated thermal behaviour of the total high-spin fraction of a SCO nanoparticle of 36 atoms for different shapes: square 6x6 (with a surface/volume ratio t=0.56) and rectangles: 9 x 4 (t=0.61), 12 x 3 (t=0.72), 18 x 2 (t=1, all the molecules are located at the surface). (b) A linear plot showing the perfect correlation between the transition temperature and the surface/volume ratio, t. The computational parameters are: Δ/k_B = 1300 K, G/k_B = 172.7 K, J/k_B = 15 K, L/k_B= 120 K, ln(g) = 6.01

3.3. Size Effects at 3D

A similar study as that of 2D is performed here for the 3D case. The computations are realized using MCM simulations on cubic nanoparticles containing 64 (4^3), 125 (5^3), 512 (8^3), 1728 (12^3), 36^3 and 48^3 particles for the same set of the model parameters. A bistability is observed for a nanoparticle of 4^3=64 molecules (mainly due to surface effects), which vanishes at higher dimensions, almost from 6^3 until 11^3 particles, before to re-appear again (due to bulk effects) from the size 12^3.

Conclusion

In this communication, we studied the effect of the size and shape of the SCO nanoparticles on their thermal bistability features. The studies were performed exactly using the entropic sampling method for the small nanoparticles and extended to bigger samples using MC simulations. For both 2D and 3D configurations, we confirmed the existence of a re-entrant phenomenon in the bistability characteristics of the nanoparticles as function of their size, in excellent agreement with recent experimental findings [1]. Furthermore, we demonstrated that the control of the shape of the SCO nanoparticles allows the control of the number of SCO atoms at the surface, thus affecting considerably their thermal properties, and so it may pave the way to the enhancement of their switching properties at small scales.

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