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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.

1. 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 [18–20] 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 nanoparticules 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 45–50 nm for the $[Fe(NH_2trz)_3](Br)_2 \cdot 3H_2O$ (NH_2trz =4-amino-1,2,4-triazole) SCO system, while Forestier et al. [42] have found a critical size value of ~30 nm. Much more smaller sizes of about ~5 nm [43] were also reported, reviving the debate, and making theoretical studies, to clarify the situation, highly desired. Recently Peng et al. [44] have shown experimentally,

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using magnetic investigations, the existence of a re-entrance behavior on small (few nanometer size-scale) spin-crossover particles: when decreasing the size from 110 nm 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: Section 2 presents the model, the results and the discussion of our investigations, and in Section 3, we conclude.

2. 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:

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

where, Δ 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 σ_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. Fig. 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, $\Delta/k_B = 840$ K, $J/k_B = 10$ K, $G/k_B = 115$ K, $\ln(g) = 6.9$ (leading to a molar entropy change $\Delta S \approx 56$ J K^{-1} 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 $T_{1/2} = \frac{\Delta}{k_B \ln g} = 121.7$ K remains size-independent.

Fig. 2a displays the associated phase diagram Δ/k_B as function of T for two values of size, $N = 30$ (5×6) and $N = 16$ (4×4). Let's consider the case $N = 30$. For a compound with Δ/k_B higher than

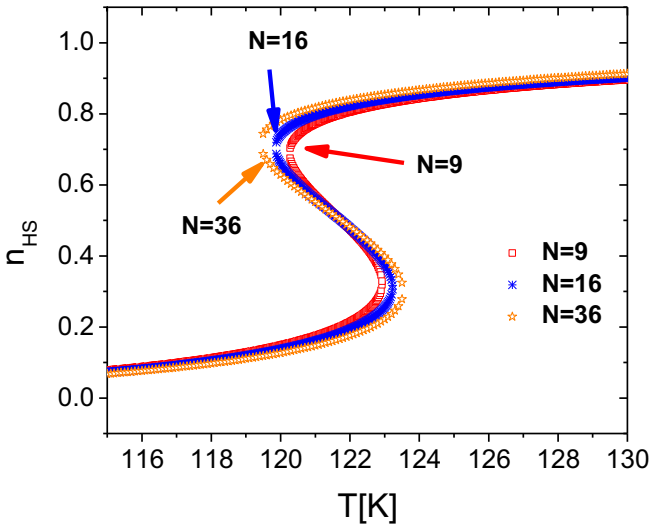

Fig. 1. Simulated thermal dependence of the HS fraction for 2D SCO system for three numbers of molecules, showing the dependence of the thermal hysteresis on size. Parameters values, used in calculations, are: $\Delta/k_B = 840$ K, $J/k_B = 10$ K, $G/k_B = 115$ K, $L/k_B = 0$ K, $\ln(g) = 6.9$.

the critical ligand field value, $\Delta_C/k_B = 997$ 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 Δ/k_B decreases to the extent that Δ/k_B becomes smaller than the critical value Δ_C/k_B, which drives the appearance of the thermal hysteresis.

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 Δ/k_B-values. It is important to notice that the critical value of energy gap increases with N till saturation, which occurs for $\Delta_C/k_B \sim 1000$ K, corresponding more or less to Δ_C/k_B value at the thermodynamic limit.

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 shown 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.

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