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On the origin of multi-step spin transition behaviour in 1D nanoparticles

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Abstract. To investigate the spin state switching mechanism in spin crossover (SCO) nanoparticles, a special attention is given to three-step thermally induced SCO behavior in 1D chains. An additional term is included in the standard Ising-like Hamiltonian to account for the border interaction between SCO molecules and its local environment. It is shown that this additional interaction, together with the short range interaction, drives the multi-steps thermal hysteretic behavior in 1D SCO systems. The relation between a polymeric matrix and this particular multi-step SCO phenomenon is discussed accordingly. Finally, the environmental influence on the SCO system's size is analyzed as well.

1 Introduction

The last years have brought new directions regarding the study of Fe^{II} spin crossover (SCO) complexes, one of these being the synthesis of switchable nanoparticles [1]. Investigating these materials at a reduced scale became a priority, urged by the necessity to assess their potential use as active elements in potential nanoelectronic and spintronic devices. Besides the expected applications of SCO nanomaterials, their fascinating switching phenomenon under various stimuli (temperature, pressure, magnetic field, light irradiation) [2,3] has drawn a considerable interest over the years from both physicists and chemists communities [4,5]. Indeed, in the last years several outstanding achievements have been reported with regards to the synthesis of SCO materials in various forms, such as: nanoparticles with different shapes and aspect ratio, SCO composites systems, SCO nanoparticles embedded in various matrix (polymeric matrix, silica matrix, MCM-41, etc.) or host-guest SCO structures [6–12].

The role of cooperativity in SCO materials has attracted great interest from unusual observations revealed experimentally [13–29]. The origin of cooperativity is assigned to elastic interactions between neighboring switching molecules and as a function of the interaction strength among molecules and/or of the lattice architecture, the spin transition (ST) curve can display a variety of shapes which can be gradual, abrupt, or stepwise [3]. Increasing the strength of these interactions, the cooperative phenomena between the spin state changing molecules can lead to a hysteretic behavior. Therefore, the coupling strength between the SCO molecules and between the SCO and the environment play an important role on the ST behavior. In the last years a special attention has been paid to the two-step behavior which was attributed to a synergistic effect between intra-molecular interactions favouring the mixed-spin state and intermolecular interactions favouring like-spin species domains. In the last five years, several coordination complexes have been shown to present a ST occurring in three steps [17–19]. Although the origin of the two-step behavior is rather clear, the origin of the three-step behavior is far from being fully understood. However, there is clear evidence that this stepwise behavior should be governed by both matrix (i.e. surface effect) and long-range interaction effects.

In this paper, we present a theoretical study on the physical origin of the three-step behavior in 1D SCO systems based on an Ising-like model [20,29,30]. Although this behavior has been experimentally observed in 2D and 3D SCO systems [17–19] and not yet for 1D systems, the physical interpretation from the analysis of the simulations performed on the 1D system can be extended to 2D and 3D SCO systems, and therefore be of interest for comparison to experiments.

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The Ising-like model with short-range (J) and long-range interactions (G) [20], presented in Section 2, has been used in several studies to reproduce different experimental behaviors such as a one-step transition [20–22] or a two-step [23] transition, with or without hysteresis. The two step SCO curve was attributed to the interplay between an antiferromagnetic (AF) short-range interaction and a ferromagnetic (F) long-range interaction. Example of two-step transition has been also reported as a consequence of binuclear molecules [28] or two-sublattices [2,29].

2 The model

The Ising-like model has first been introduced by Wajnflasz and Pick [30], in which only short interactions were considered. Later on Bousseksou et al. [29] made a thorough analysis of this model in the mean field approach. In order to be able to reproduce hysteresis in 1D compounds, within the frame of this Ising-like model, Linares et al. [20] have introduced, besides the short interaction, also a long range one in the Hamiltonian. In fact, by the deformation of the spin changing molecules, an elastic coupling leads to a long range interaction and a strong bonding between the molecules leads to a short range interaction. Thus, the long range interaction introduced in the Hamiltonian are always ferromagnetic-type with a positive G while the short range interactions can be either ferro or anti-ferro magnetic-type. In this work, in order to take into account the matrix effect, we have added an additional interaction parameter which accounts for the SCO molecules behavior within the environment (matrix effect), that is termed, the matrix interaction P. This interaction is assumed to act on the molecules localized at both ends of the 1D SCO system. In this case, the system's Hamiltonian can be written as follows:

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

where the first term represents the temperature dependent field, the second and third terms are describing the long- and short-range interactions, respectively. The last term describes the interaction of the SCO system with the matrix. Δ is the energy gap between the high-spin (HS) and low-spin (LS) states, and g is the degeneracy ratio of the two states.

Since the ratio of HS state n_{HS} as a function of the pseudo-spin variable can be expressed by

$$n_{\mathrm{HS}} = (1 + \langle \sigma \rangle)/2 \quad (2)$$

and appears self-dependent of $\langle \sigma \rangle$, we propose an analytical treatment using a new expression of n_{HS} based on the bisection technique.

Thus, the system's Hamiltonian could be expressed as a function of the dimensionless macroscopic variables:

$$m = \sum_{j=1,N} \sigma_j \quad (3)$$

$$s = \sum\nolimits_{\langle i,j \rangle} \sigma_i \sigma_j \quad (4)$$

and

$$c = \langle \sigma_1 + \sigma_N \rangle \quad (5)$$

(herein σ_1 and σ_N represent the spin operator associated to the first and the last molecule in the molecular chain):

$$H = \left(\frac{\Delta - k_B T \ln g}{2} - G \langle \sigma \rangle \right) m - Js - Pc. \quad (6)$$

The canonical expression of $\langle \sigma \rangle$ can be constructed in terms of the above dimensionless quantities:

$$\langle \sigma \rangle = \frac{\sum_{j=1,NL} \frac{m_j}{N} d(m_j s_j c_j) \exp\left(-\frac{1}{k_B T} (-h_f m_j - J s_j - P c_j) \right)}{\sum_{j=1,NL} d(m_j s_j c_j) \exp\left(-\frac{1}{k_B T} (-h_f m_j - J s_j - P c_j) \right)}, \quad (7)$$

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

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

Since $d(m,s,c)$ is the degeneracy of each state $\langle m, s, c \rangle$, we are able to generate all the system configurations building by this way, the states distributions of the molecular system.

3 Results and discussion

Upon considering open boundary conditions and following and applying numeric calculation to equation (7) as bisection technique, the curves from Figures 1 and 2 were obtained where n_{HS} resulting from equation (2). Moreover we discuss in the rest of the paper some simulations regarding the behavior of a 1D system using the values of parameters Δ, $\ln(g)$ in the range of those of SCO compounds.

From a previous numerical study [31,32] it was shown that a stepwise behavior could be obtained in 3D SCO systems by taking into account negative short-range interactions (anti-ferromagnetic-like interactions) and positive long-range interactions (ferromagnetic-like interactions). Following similar conditions, it is further considered in this work, that the coupling between the matrix and the edge molecules is ferromagnetic-like (positive).

The results on the influence of the SCO-matrix interaction strength are reported in Figure 1. By increasing the

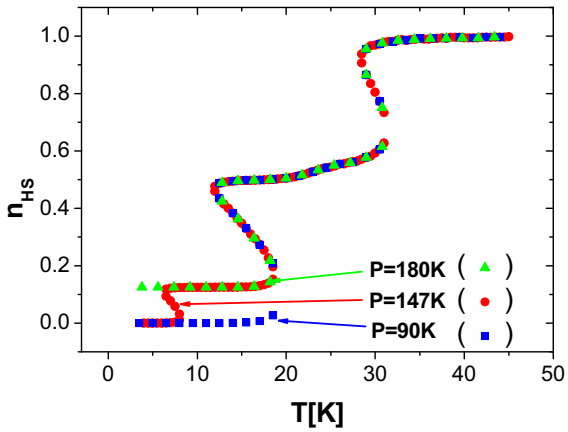

Fig. 1. Thermal evolution of the HS molar fraction n_{HS} in a 1D SCO system embedded into a matrix for different matrix interaction strength: square (P/k_B = 90 K), circle (P/k_B = 147 K) and triangle (P/k_B = 180 K). The parameter values are: N = 16 molecules, Δ/k_B = 240 K, $\ln(g)$ = 9.5, G/k_B = 120 K, and $J/k_B = -43$ K.

value of P, the 1D SCO system goes from a complete two-step behavior ($P/k_B = 90$ K, with k_B the Boltzmann constant) to a complete three-step behavior for an interaction strength between the matrix and the boundary molecules given by $P/k_B = 147$ K. Moreover, an incomplete two-step transitionis obtained for higher values of $P/k_B = 180$ K. These results are to be compared to the incomplete behavior induced by the SCO-matrix interaction strength that were recently reported by Stoleriu et al. [33] in the framework of the mechano-elastic model. In their paper, it was concluded that the nanoparticle system behavior is affected drastically by the matrix environment upon decreasing the nanoparticles system's size. Atitoaie et al. [34] and Muraoka et al. [35] have also studied the effect of the environment on the SCO behavior.

In the past years, particular attention was paid to the influence of size effect in the frame of the nanostructuration of SCO complexes [1]. Since the hysteretic behavior of the SCO systems is strongly affected by the decrease in the number of molecules, many studies were reported on the critical size, under which the SCO system losses its hysteretic properties. Rotaru et al. [36] studied a series of nanoparticles of the surfacted $[Fe(NH_2trz)_3]Br_2 \cdot 3H_2O$ (NH_2trz = 4-amino-1,2,4-triazole) SCO complex, with various mean sizes (30–110 nm) using first-order reversal curves (FORC). They have shown that the critical size is around 45–50 nm. On the other hand, SCO systems with a critical size below 10 nm have been also reported [6]. The size effect in SCO systems exhibiting a three-step behavior has however not been studied so far. For this reason, we present in the following, a study on the size influence on 1D SCO system exhibiting a stepwise thermal behavior.

In Figure 2, the simulated thermal behavior of the HS fraction is shown for various numbers of molecules. We show that, when the SCO system size consists of a high number of interacting molecules, the thermal behavior of the 1D SCO system, depending on the matrix interaction strength, can exhibit both two-step and three-step ST and both complete or incomplete transition. However, when the system's size is decreasing, the coupling between the edge molecules with the matrix becomes more important and the synergistic effect between intra-molecular interactions favors the mixed-spin state configuration. Thus, with the decrease of the system's size, the SCO particles embedded into a matrix can exhibit even a four-step behavior. As it was expected, the decrease of the system's size also affects the increase of the residual HS fraction, for high values of the matrix interaction parameter. Another feature that was observed with the decrease of the number of molecules, is a shift of the equilibrium temperature $T_{1/2}$ to low temperatures, in good agreement with the experimental data reported in reference [7].

Because in our model the edge atoms are not blocked in the HS state, it is difficult to give an evolution of $T_{1/2}$ as a function of all the system's parameters (i.e. Δ, $\ln(g)$, J, G and P). A particular aspect which should be noted here is the fact that different cooperative effects at small nanoparticles sizes were obtained, in good agreement with the results reported by Tokarev et al. [37] for of $[Fe(NH_2trz)_3](tosylate)_2$ nanoparticles of 3–4 nm in size.

In Figure 3 we show the case where P as well as J, the short range interaction are 0, together with the case with P/k_B = 147 K and $J/k_B = -43$ K. It is clear from this figure that the multi-steps hysteresis transition originates from the interaction of the border SCO molecules with the local environment together with an antiferromagnetic-type short range interaction.

The value of the parameter P, which is a "long-range interaction" between the matrix and the SCO at the surface, is of the same order with the long-range interaction parameter G.

The role of the long-range (G) as well as the short-range interaction on the thermal behavior are presented in Figures 4 and 5, respectively. For a high value of the long-range interaction, three-step hysteretic behavior can be reproduced, however the hysteresis disappears, as we expected, for small values of the long-range interaction.

The short-range interaction strength plays an important role on the stepwise behavior. Thus, when the short-range interaction strength dominates the other two interactions parameters, i.e. long-range and the matrix interaction parameters, the stepwise behavior is more pronounced. For a small value of short-range interaction, the stepwise behavior can be masked by a macroscopic one-step behavior.

4 Conclusions

This study demonstrates that the LS-HS transition triggered within an Ising-like model frame refined with a border SCO-matrix interactions, provides a qualitative insight on the physical origin of the cooperative phenomenon in 1D SCO systems embedded into a matrix.

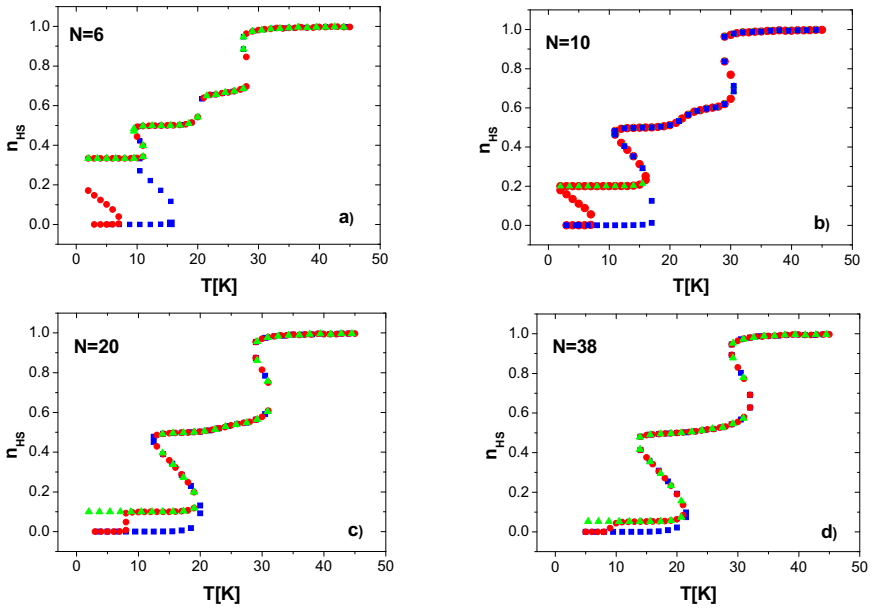

Fig. 2. Evolution of the HS molar fraction n_{HS} as a function of temperature, for various numbers of molecules: (a) $N = 6$ molecules, (b) $N = 10$ molecules, (c) $N = 20$ molecules, (d) $N = 38$ molecules for different polymeric-interactions strength: square ($P/k_B = 90$ K), circle ($\mathrm{P}/k_B = 147$ K) and triangle ($P/k_B = 180$ K). The computational parameters are: $\Delta/k_B = 240$ K, $\ln(g) = 9.5$, $G/k_B = 120$ K, and $J/k_B = -43$ K.

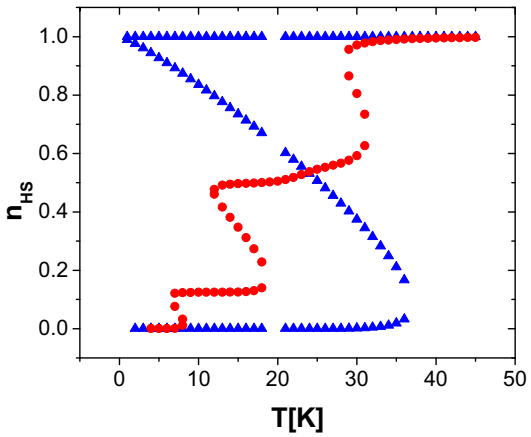

Fig. 3. Evolution of the HS molar fraction n_{HS} as a function of temperature, for the case: circle ($P/k_B = 147$ K, $J/k_B = -43$ K) and triangle ($P/k_B = 0$ K, $J/k_B = 0$ K). The computational parameters are: $N = 16$, $\Delta/k_B = 240$ K, $\ln(g) = 9.5$ and $G/k_B = 120$ K.

The main characteristic of this work is in the consideration of three types of interactions (short-range, long-range and SCO-matrix) which are responsible for the multi-step transitions. These strong cooperative effects which are shown to occur even in small-sized nanoparticles systems, confirm the results reported recently [6–8,35,37–40], that, depending on the compounds characteristics, hysteretic behavior is observed in such systems.

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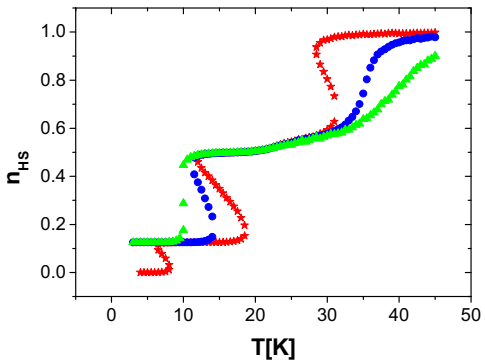

Fig. 4. Evolution of molecules in the HS state n_{HS} as a function of temperature, for a 1D system $N = 16$ molecules, for different long range-interactions strength: $G/k_B = 40$ K (triangle), $G/k_B = 80$ K (circles), $G/k_B = 120$ K (star). The parameter values are $\Delta/k_B = 240$ K, $\ln(g) = 9.5$, $J/k_B = -43$ K, and $P/k_B = 147$ K.

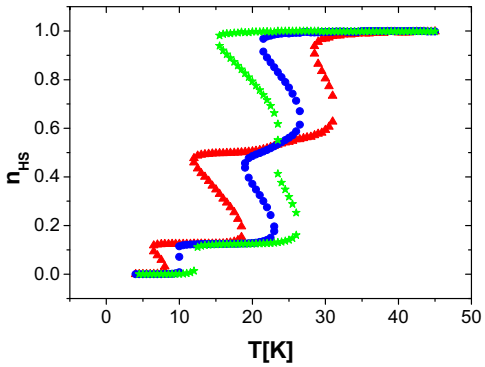

Fig. 5. Evolution of molecules in the HS state n_{HS} as a function of temperature, for a 1D system $N = 16$ molecules, for different long short-interactions strength: $J/k_B = -43$ K (triangle), $J/k_B = -30$ K (circle) and $J/k_B = -20$ K (star). The parameter values are $\Delta/k_B = 240$ K, $\ln(g) = 9.5$, $G/k_B = 120$ K, and $P/k_B = 147$ K.

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