PhD Thesis Highlights

"Contributions to the study of hysteresis and relaxation processes in spin transition systems"

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Spin crossover compounds are a particular category of molecular magnetic materials, being in the recent years in the focus of the scientific community. The scientific interest on these materials comes from their bistable properties. The spin transition compounds are formed from a central transitional metal ion (Fe(II), Fe(III), Co(II), Co(III), Mn(II), Mn(III), Cr(II)), surrounded by ligands in an octahedral geometry. A spin crossover compound can have two distinct magnetic states, switchable through external perturbations, like temperature and pressure variation, light irradiation or by applied magnetic fields. The optical and magnetic properties of these materials also change with their spin state. The spin state of the molecule in which the total spin is maximum is named "high spin state (HS)" and has paramagnetic properties, while the state in which the total spin is minimum is named "low spin state (LS)" and has diamagnetic properties. The transition between the high spin state and the low spin state produces also structural and optical changes, like changes in volume and color of the compounds. The recent achievements of the synthesis chemistry in order to obtain a broad range of spin crossover compounds with various properties, from thin films and nanoparticles toward micro- and nanowires with room temperature thermal transition, opened the way to a broad class of applications in recording media industry, in the development of a new class of solid state thermal, pressure and thermocromic sensors, molecular actuators and OLED devices.

The first chapter of the thesis is putting forward a short general presentation of the spin crossover materials and the physical origin of molecular processes that are on the basis of the two spin states and also the way that these processes are influencing the structural, magnetic and optical properties of these compounds. The first chapter also presents the most common application and the newest research perspectives using spin transition compounds.

This thesis focuses on the investigation of the spin state transitions produced by temperature variation. Very high temperatures are favoring the high spin state, while low temperatures are causing the low spin state. The characteristics of the thermal transitions depend on the strength of intermolecular interactions that are specific for the studied spin crossover material. For a diluted compound, where the distance between the molecules is

bigger and therefore are not interacting with each other, the transition will be gradual, continuous and anhisteretic. On the other hand, if there is cooperativity in the system and the molecules are interacting with each other, then the transition will present a thermal hysteresis. The width of the hysteresis loop will be proportional with the interactions strength. These intermolecular interactions have an elastic origin and are caused by the volume variations that are produced during transition, generating a relocation of the molecules within the lattice.

The second chapter presents a chronological review of the most important theoretical models that have been developed for the study of spin crossover thermal hysteresis loops and their characteristics. Even though a broad spectrum of models has been elaborated, the most frequent ones that are used for the investigation of thermal transition are represented by the Ising-like models. These models have been improved step-by-step, taking into account both long range and short range interactions in order to fit better the experimental results. The Ising-like models are in the central interest of this chapter, being the backbone of the models developed for the investigation of spin transition nanoparticles thermal hysteresis that has been further analyzed within the thesis. Moreover, several models that explain the elastic interactions and other characteristics of thermal hysteresis loops which use different approaches have been elaborated and presented also in this chapter, like the mechano-elastic model based on the "ball and spring" concept or the atom-phonon coupling model.

The original contribution brought by the present thesis to the study of thermal transitions of spin crossover compounds is reflected starting with the third chapter, that present a dimensional study of the thermal hysteresis width and shape depending on the system size. The thermal transition presents some particular characteristics that may differ depending on the intermolecular interactions, internal and structural parameters of the studied material, the shape and dimension of the sample or the synthesizing method. Therefore, for the investigation of the thermal hysteresis it is developed an Ising-like model adapted from a previous model used by Dobrinescu et al. in order to study the relaxation of spin transition systems. The proposed Ising-like model takes into consideration both short- and long-range interactions that are specific for the interactions with the nearest neighbors and respectively with all the molecules from the system through a mediated interaction. The model is applied for both bidimensional and tridimensional spin crossover systems and it is implemented using a Monte Carlo method with Arrhenius dynamics, using the following transition probabilities:

$$\begin{cases} P_{HL} = \frac{1}{\tau} e^{\frac{-T\Delta S+\Delta}{2T}} e^{-\frac{Ea+2G<\sigma>+2J\sum\sigma_{vecini}}{k_B T}} \\ P_{LH} = \frac{1}{\tau} e^{\frac{T\Delta S-\Delta}{2T}} e^{-\frac{Ea-2G<\sigma>-2J\sum\sigma_{vecini}}{k_B T}} \end{cases} \quad (1)$$

where the term τ is a parameter chosen arbitrary that has the role of scaling the probability and the switching time, Δ is the energy difference between the two states, T is the temperature, ΔS is the entropy variation during switching and E_a is the activation energy. The term $<\sigma>$ represents the fictitious average spin of the whole system calculated, while $\sum\sigma_{vecini}$ is the sum of the nearest neighbors spins. The G and J parameters are scaling the long range respectively short range interactions. In Figure 1 there are simulated the thermal hysteresis loops for a bidimensional system of 3600 molecules and a tridimensional system with a comparable number of molecules, 3375, and the same internal parameters. It can be observed that the width of the hysteresis loop in the case of the cubic system is larger and the transition is visible more abrupt that in the case of the bidimensional system. This results are explained by the fact that in the tridimensional system the cooperativity is bigger due to the higher number of nearest neighbors (6 instead of 4).

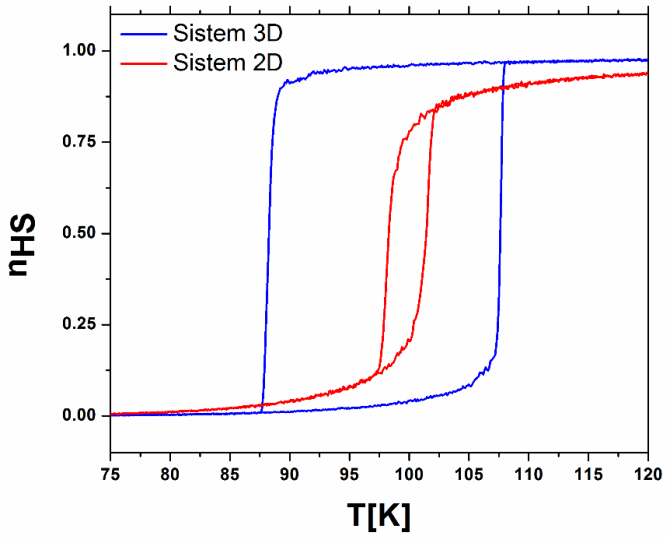

Figure 1. Thermal hysteresis loops for a 2D (red line) and 3D (blue line) spin crossover systems with the same number of particles.

The experimental measurements on the properties of thermal switching in the case of recently sinthesized spin crossover nanoparticles showed several particular characteristics of the thermal hysteresis loops that are significantly different that in the case of bulk materials. The fourth chapter proposes the first Ising-like model developed in order to explain and reproduce all the peculiar properties of nananoparticulated systems thermal transition,

starting from a series of assumtions that are taking into account the importance of the interactions between the molecules from the edges of the nanoparticles and the environment in which were sinthesized.

It has been observed that with the decreasing dimension of the nanoparticulated systems, the width of the hysteresis loop diminishes while the transition is delayed and the transition temperature also decreases, which is opposed to the case of bulk systems where the transition temperature is constant for every dimension of the system. Also, in the case of nanoparticles, even at very low temperatures, there is a significant proportion of molecules that remain in the high spin state, forming the so called residual spin fraction. In order to explain these peculiar features of the thermal hyteresis loop, it was developed an Ising-like model which takes into consideration not only the short range and long range interactions, but also a new contribution to the cooperativity of the system from the polymer matrix in which the nanoparticles are sinthesized and confined, therefore a new interaction scaled by the factor J_B between the molecules from the margins of the nanoparticle and the surrounding polymer molecules. The polymer matrix favorizes the HS state due to the tendency to oppose the volume changes, therefore the polymer particles are considered fixed and non-switchable in the HS state. In Figure 2 there are represented spin crossover nanoparticles embedded in polymer environment and it is illustrated the way in which the polymer molecules interact with the edge molecules from the nanoparticulated system.

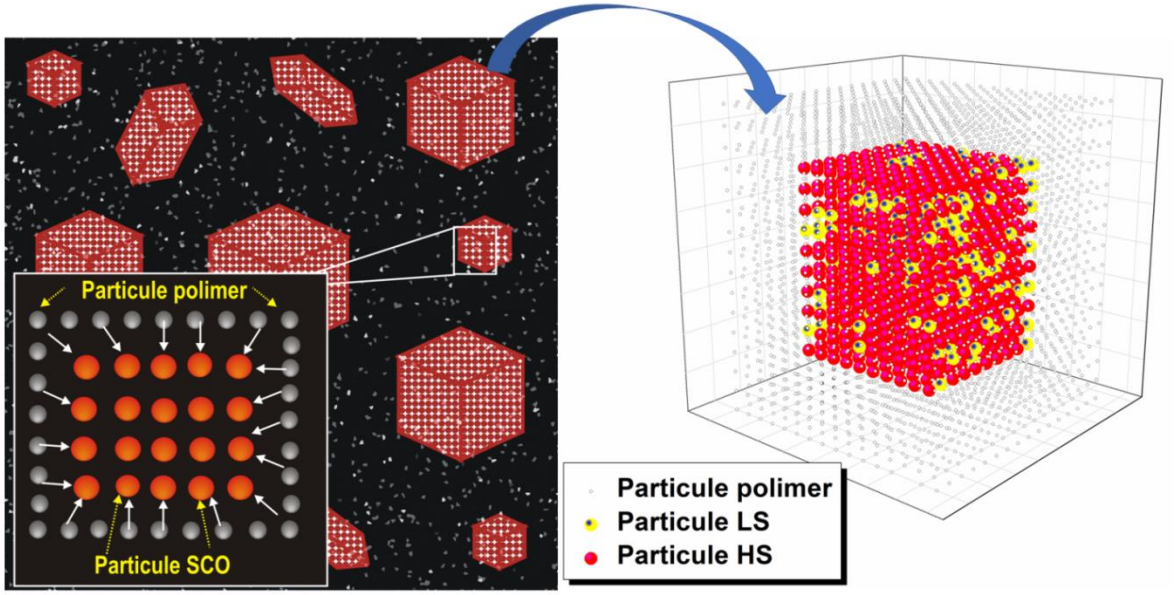

Figure 2. System of nanoparticles embedded in polymer and illustration of the edge polymer-nanoparticle interaction.

Taking into account the new assumption and the edge interactions, were computed thermal hysteresis loops for nanoparticles with different dimensions. It can be observed in Figure 3, that the transition temperatures shift toward lower values when the dimension of the nanoparticulated system diminishes, along with a significant residual spin. The smaller the size of the nanoparticle, the bigger these effects of delaying the transition and residual spin are. This can be explained by the proportion between the molecules from the edge with the ones within the nanoparticle. For smaller system this proportion is higher, therefore these effects are enhanced.

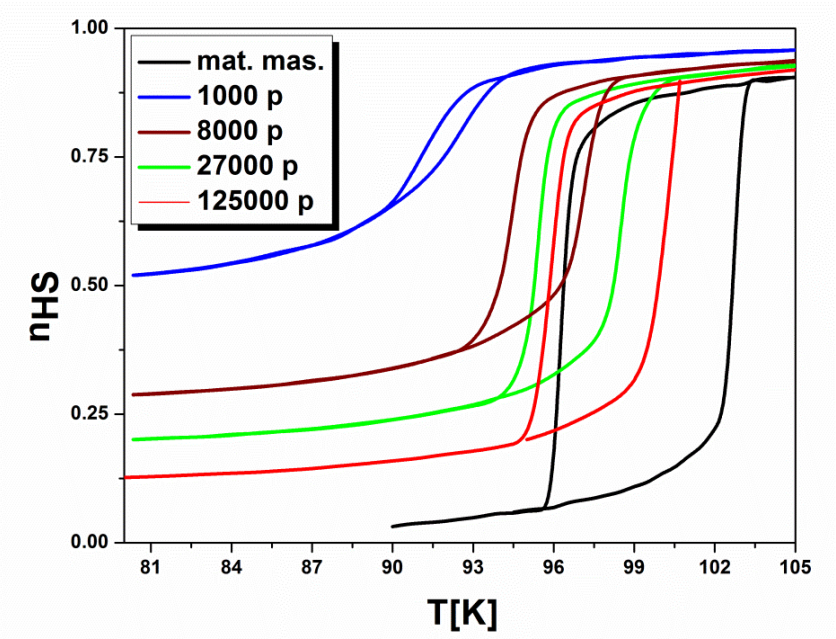

Figure 3. Thermal hysteresis loops for nanoparticles with different sizes.

On the fifth chapter it is used the FORC diagram method (First Order Reversal Curves), that is based on the special class of minor hysteresis loops – the first order reversal curves – in order to investigate the irreversible and reversible contributions to the switching process along with the kinetic effects that are significant in some spin crossover materials. The experimental analysis on spin crossover nanoparticles it is usually performed on samples that are actually systems of nanoparticles that can be characterized by a size distribution. The direct simulation of this type of systems cannot be performed due to the limit of present supercomputers, therefore this thesis proposes a method through a dissociative approach for the simulation of such systems of nanoparticles, in which the nanoparticulated systems are distributed by both their sizes and their intermolecular interaction strength. Through this method are analyzed the principal characteristics of thermal hysteresis loops for a realistic sample.

The sixth chapter proposes a dynamic analysis of transition processes in spin crossover compounds. A theoretical limit in the characterization of these spin crossover compounds is represented by the individual investigation of reversible, irreversible and kinetic components of the thermal hysteresis loops. The principal problem is that the kinetic effects cannot be separated qualitative and quantitative by the reversible processes. In this chapter it is analyzed the contribution of kinetic effects by using the FORC diagram method on systems of nanoparticles simulated with different speeds of temperature variation. Moreover, a systematic study of the thermal relaxation in the case of spin crossover bulk materials and nanoparticles is performed. This study is useful in the determination of the principal parameters that influence the time and the relaxation speed, as long as the kinetic effects represent, in fact, the competition between the speed of temperature variation and the speed of the thermal relaxation.

In conclusion, the applicability of spin crossover compounds in the development of new devices and technologies at micro- and nanoscale requires a much deeper knowledge of thermal transition processes. Therefore, it is essential the investigation of all the elements that influence the shape and the width of the spin transition thermal hysteresis loops, for both bulk and nanoparticulated materials or systems of nanoparticles, taking into account all the internal and structural parameters that are influencing the switching processes along with the cooperativity. All these investigation were performed, discussed and interpreted within the thesis.