PHYSICAL PARAMETER DISTRIBUTION IN SPIN TRANSITION SYSTEMS DERIVED FROM FORC DATA

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Spin crossover compounds show a first order phase transition that can be accompanied by a thermal hysteresis. In this paper we present the analogies between this class of substances and magnetic systems with a domain structure. We show the possibilities of study the thermal hysteresis of spin crossover solids using Preisach-type models and of the First Order Reversal Curves (FORC) method. Experimental FORC diagrams were obtained for pure and diluted spin transition system $[Fe_xZn_{1-x}(btr)_2(NCS)_2]H_2O$, where x governs, through cooperative interactions, the width of the thermal hysteresis loops. A parametrical identification of the distributions corresponding to inter-domains interactions domain size was performed also using an Ising like model.

1. Introduction

Spin transition compounds are a class of inorganic coordination complexes that contain central metal ions of $3d^4$-$3d^7$ electron configurations, situated in an octahedral ligand field determining the existence of two possible spin states [1]. The diamagnetic low spin state (LS) is the ground state at low temperature, while the paramagnetic high spin state (HS) is the stable state at high temperatures. The change of electronic state in such a complex between LS and HS when the temperature is modified is known as spin transition phenomenon. The spin transition is accompanied by changes of magnetic, optical and structural properties of the system. If N_{HS} and N_{LS} are the number of molecules in HS respectively LS the parameter that characterises the macroscopic state of the system is the high spin fraction, denoted as $n_{HS}= N_{HS}/(N_{HS}+N_{LS})$.

The spin transition principles can be understood by the way of simple thermodynamical considerations. The variation of the free energy Gibbs is given by:

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

The temperature for which $N_{HS}=N_{LS}$ is obtained when $\Delta G=0$, so that:

$$T_{1/2} = \frac{\Delta H}{\Delta S} = \frac{\Delta_0}{k_B \ln g} \tag{2}$$

where Δ_0 is the energy difference between the HS and LS states of independent molecules, and g the degeneracy ratio.

The basic description of the spin conversion is the following: at low temperature, under $T_{1/2}$, the enthalpy factor dominates, ΔG is positive and the low spin state is the stable one. When the temperature is higher, the entropy factor dominates, ΔG is negative and the high spin state is stable.

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The interactions induce a steeper transition, accompanied by hysteresis. In terms of the molecular configurational diagram (Fig. 1), the interactions determine a change in the energy difference between the wells associated with the two spin states: on increasing the population on the HS state, the energy difference Δ_0 diminishes (so the transition temperature (eq. 2) is different if the temperature is increased or decreased). We can say then that the interactions induce a static stabilization of the populated state which may transform a continuous thermal population effect into a first order transition.
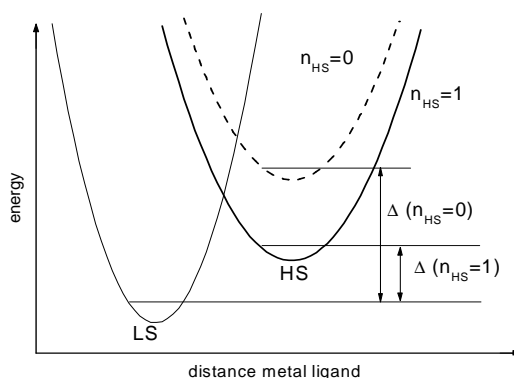

Fig. 1. The configurational diagram of a spin crossover molecule: the adiabatic energies in each spin state, as a function of metal-ligand distance.

The spin transition was described by several models based on the concept of fictitious spins (Ising-like [2]), or involving short-range and long-range interactions [3], and a clear analogy with magnetic models has been developed. This analogy was extended to the concept of spin-like domains during the switching processes [4].

Recently, in magnetism it was introduced the First Order Reversal Curves (FORC) diagram method, as a global characterization method for magnetic systems. In [5] we adapted for the first time this method to characterize the spin transition solids and we obtained a first evidence that bias and coercitivity are relevant parameters for the description of collective behavior of spin-like domains. There it was established that the bias reflects the effect of internal stresses (inter-domain interactions) while the coercivity corresponds to the strength of intra-domain interactions. An essential problem of FORC diagram method applied to thermal and magnetic hysteresis, is finding a physical meaning of diagram.

In present paper, using an Ising-like model [2] to explain the thermal hysteresis of a single grain (the system that we study has also a granular structure) and the techniques developed previously in Preisach models, we simulate the FORC diagram of the model. By the way of parametrical procedures of identification, we obtained the physical parameters that describe optimal, in the frame of considered hypotheses, the thermal hysteresis of physical system and its experimental FORC diagram.

2. Preisach model. FORC diagram method

Some times ago, it was suggested that the spin transition occurs through spin-like domains, including molecules in the same spin state [4]. It is known that the sufficient and necessary conditions for applying the classical Preisach model [6] are the wiping-out property – which essential means that minor loops are closing exactly and the final state is identical with the initial one – and the congruency property that means that shapes and areas of all minor loops between the same extreme temperatures are equal.

The fundamental element in Preisach model is the hysteron characterised by a rectangular hysteresis loop. In magnetic hysteresis this is defined by the switch fields H_α H_β (fig.2a). The shift of the loop along the field axis it is known as bias field and can be connected with the interaction field. In the case of thermal hysteresys of spin crossover solids, the switching temperatures T_α T_β may have only positive values (fig.2b). The thermal hysterons bias is distributed in real systems. The Preisach distribution $P(H_\alpha, H_\beta.)$ from magnetic systems become $P(T_\alpha, T_\beta)$ in the case of thermal hysteresis for spin crossover solids.

In paper [7] – we applied the classical Preisach model to reproduce the major and minor thermal hysteresis loops in the high spin-low spin transition for a pure compound (x=1). We determined the Gaussian Preisach distributions of transitions temperatures which fitted the experimental data. For diluted compounds, the model must include a distribution of concentration x due to the defaults of the crystals obtained from solutions.
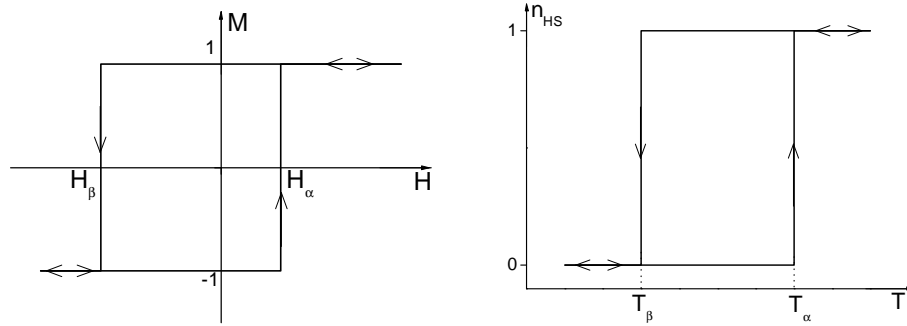
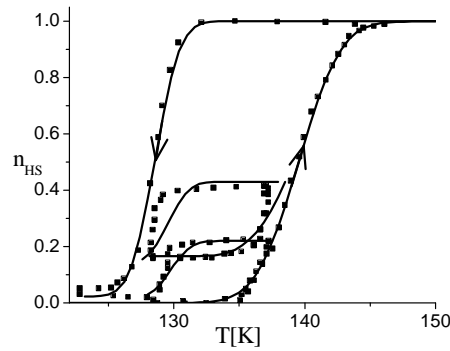Fig. 2. The hysterons corresponding to the magnetic hysteresis (left) and to spin crossover solids hysteresis (right).

Fig. 3. $[Fe_xNi_{1-x}(btr)_2(NCS)_2]H_2O$, x=0.66, Major and minor hysteresis loops. Simulations using the Preisach model with a gaussian distribution of compositions. σ_x=0.05

In Fig. 3 we present the experimental data for the spin crossover system, $[Fe_{0.66}Ni_{0.34}(btr)_2(NCS)_2]H_2O$, together with the best fit with the Preisach model.

The Preisach-type models can be applied successfully for the thermal hysteresis; but the results depend in a certain manner on the characteristics of the model (moving parameter, gaussian distribution, reversible part). A more general method, model-independent, is the FORC method [8], used previously to analyse magnetic systems [9]. Replacing the magnetic field with the temperature, one can study the evolution of the spin domains associated to the thermal hysteresis cycle in the spin transition solids [5].

This method consists in the analysis of a series of partial hysteresis curve of FORC type. The measure of a FORC for the spin transition compounds starts at a sufficient high temperature where the high spin domain structure is saturated. Then we decrease the temperature until a certain variable temperature that is the reversal temperature, denoted here as T_A. A FORC (fig.4) is composed by the set of experimental high fraction values corresponding to the temperatures T_B measured during the increasing the temperature until reaching the saturation. By repeating this procedure for different reversal temperatures, we obtained a series of FORC's.

The FORC distribution, that can provide information about the distributions of different parameters in the sample, is defined as the second mixed derivative of the high spin fraction for all these curves:

$$\rho(T_A, T_B) = -\frac{1}{2}\frac{\partial^2 n_{HS}(T_A, T_B)}{\partial T_A \partial T_B} \tag{3}$$

The contour plot of distribution $\rho(T_A, T_B)$ is known as FORC diagram.

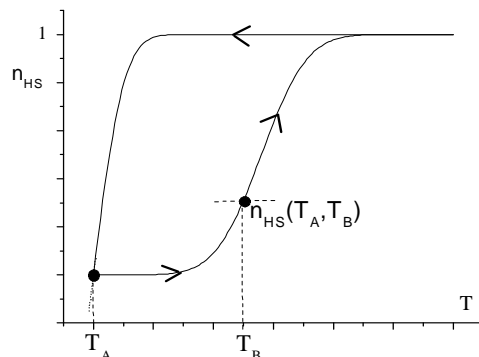A similar procedure can be applied starting on the heating branch of the thermal hysteresis loop.

Fig. 4. Definition of a FORC in the warming mode. After the high spin domain structure is saturated, the temperature is lowered and increased again. The corresponding high spin values constitute the FORC

3. Experimental data

The samples were crystalline powder [10], cycled several times, from room temperature to 77K to obtain a constant texture of the sample and reproducible hysteresis loops. The LS state is dark red while the HS state is white, so the spin transition can be easily detected by optical measurements, in our case reflectivity. We performed reflectivity (using the light provided by a tungsten halogen lamp, through interferential filters) and magnetization measurements (SQUID magnetometer). The reflectivity measurements provide information about the surface of the investigated compound, while the magnetization measurements scan the bulk behavior, but if the sample is thin enough and an appropriate wavelength is used for reflectivity they give compatible results [11]. The samples were as thin as possible and about 1 mg weight and the temperature was scanned every 0.5K. In Fig. 5, we present the FORCs in the warming mode $[Fe_xZn_{1-x}(btr)_2(NCS)_2]H_2O$, for x=1 and x=0.4. As observed in previous works (see for instance [12]) the major hysteresis loops for diluted compound move towards lower temperatures, as the impurities stabilise the high spin state and the hysteresis width diminishes, as the interactions decrease.
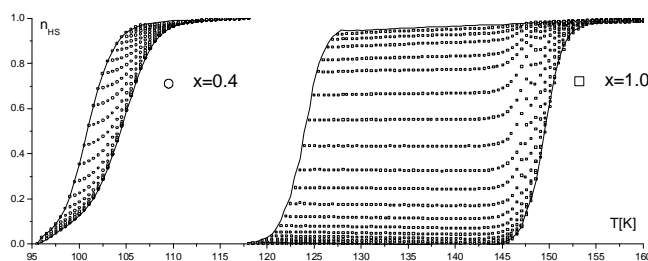

Fig. 5. $[Fe_xZn_{1-x}(btr)_2(NCS)_2]H_2O$: Experimental FORCs for a) the pure compound (x=1, squares); b) for diluted compound (x=0.4, circles).

4. Simulated FORC diagram

A basic interpretation of the FORCs consist in getting directly form the experimental data the FORC distributions (that corresponds to the Preisach distributions if the wiping-out and congruency property are obeyed), as in Fig. 5. As we have discussed this aspect in [5], we shall refer here only to the possibilities to obtain the distributions of physical parameters implied in spin transition using FORCs and an Ising-like model.

Usually, the quasi-static proprieties of spin transition compounds are modulated with an Ising-like model (the main difference with true Ising model is the degeneracy ratio g≠1) [13]. It is based on a simplification of the complete vibronic level scheme in the adiabatic approximation, by considering two-level interacting units, with different energies and degeneracies.

In the mean-field approach the one-site hamiltonian is written:

$$h_i = \frac{\Delta_0}{2}\sigma_i - J\sigma_i \rangle \sigma \langle \tag{4}$$

where Δ_0 is the energy gap («fictitious field») between the two states LS and HS of uninteracting molecules, σ_i is the fictitious spin operators with eigenvalues ±1, and J is the interaction parameter, including the effect of all neighbours. The high spin fraction can be expressed as a function of the «fictitious magnetisation» $<\sigma>$ as:

$$n_{HS} = \frac{1+\langle\sigma\rangle}{2} \tag{5}$$

Taking into account the two different degeneracies of the two spin states g_{LS} and g_{HS}, and a temperature dependent energy gap (« fictitious effective field »), the Ising-like hamiltonian can be written in the Ising equivalent form for all the molecules [14]:

$$h_i = \sum_i \left(\frac{\Delta}{2} - \frac{k_B T}{2}\ln g - J<\sigma> \right)\sigma_i, \tag{6}$$

where $g=g_{HS}/g_{LS}$ is the « effective » degeneracy ratio and can be expressed as a function of the entropy change upon conversion ΔS : $g=\exp(\Delta S /R)$.
The fictitious magnetisation can be expressed in the form:

$$\langle\sigma\rangle = \tanh\left[-\frac{1}{k_B T}\left(-J\langle\sigma\rangle + \frac{\Delta}{2} - \frac{k_B T}{2}\ln g \right) \right] \tag{7}$$

By solving this equation, we can easily obtain $<\sigma>$ for each temperature and in the end, only the major hysteresis loop (Fig. 6); the states from inside the hysteresis loop can not be reach by the system and the FORC can't be simulated. The experimental observation of the minor cycles implies the existence of a distribution of the physical parameters Δ and J. Every pair of (Δ,J) gives an elementary loop, that is approximate with thermal hysteron if the reversible part observed in fig 6 is neglected, and the superposition of all, allows to make the minors loops.
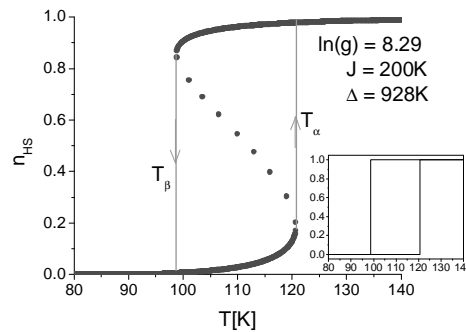

Fig. 6. Hysteresis loop simulated for a pair off physical parameters ($\Delta=928K,J=200K$). Insert: rectangular loop that is defined by the switching temperatures, and used to simulate FORCs.

Using only one hysteron it's impossible to obtaine minor loops, so to describe experimental data we have to take a distribution of parameters J and Δ and we proposed from the beginning a double Gaussian distribution

$$P(\Delta,J) = \frac{1}{2\pi\sigma_\Delta\sigma_J}\exp\left(-\frac{(\Delta - \Delta_m)^2}{2\sigma_\Delta^2} \right)\exp\left(-\frac{(J - J_m)^2}{2\sigma_J^2} \right), \tag{8}$$

where Δ_m is the average energy gap, J_m the average interaction and σ_Δ, σ_J the standard deviations. We want to see if it's possible to obtain a diagram similar with experimental FORC diagram.

With the distribution mentioned above we have divided the (J,Δ) plane in equal small enough regions. To every region we assign a weight that corresponds to distribution (8) and a cycle described in the beginning of this section, making the assumption that a region is characterised only by a single J and Δ. These weights are associated in Preisach plane to the point of coordinates (T_α,T_β) and, in this way, a discrete Preisach distribution it's defined. Using Preisach model technics, one can calculate FORC curves

and diagram. In Fig. 7 one presents simulated FORC curves (experimental FORC are in fig. 5) experimental diagram and the simulated one.
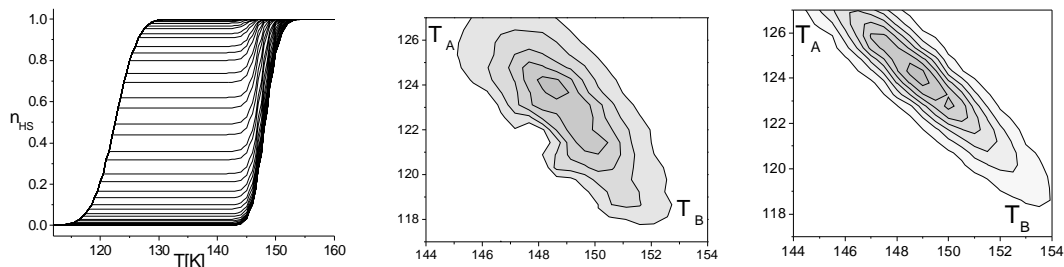

Fig. 7. (a) Simulated FORCs for x=1; (b) FORC diagrams for the pure compound x=1.0 from experimental data; (c) simulated FORC. Parameters values used in simulations: Δ_m=1250K, J_m=250K, σ_Δ=5K, σ_J=15K.

5. Conclusions

In the present paper we developed o procedure to connect the physical parameters (J,Δ) and their distribution with parameters that can be used to simulate thermal hysteresis and FORC curves. For pure compound (x=1.0) the double independent Gaussians distribution of J and Δ gives a FORC diagram that fit the experimental one. Supplementary problems are encounter when x<1.0 for which the reversible part have to be consider in simulations.

In this paper we have presented a solution to the direct problem, that is, to calculate the FORC diagram from a known distribution of physical parameters. In a future paper we shall discuss the inverse problem, that is, to find the distribution of characteristic physical parameters for a given system from the experimental FORC diagram.

Acknowledgements

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