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Study of impurities effect in spin crossover compounds using first order reversal curves (FORC) method

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Abstract

Using the FORC method, we present in this communication a study on the diluted spin transition materials with the formula $[Fe_xM_{1-x}(btr)_2(NCS)_2]\cdot H_2O$ with M = Zn, Co and Ni. We compare the evolution of distributions obtained for different dilutions with the three impurities and we notice that these distributions depend not only on the dilution $(1-x)$ but also on the impurity used.

The statistical analysis shows that the maximum values of the distributions are close to a linear dependence for Zn and Co. The impurity that does not obey this dependence is Ni, which volume is close to the average volumes of high spin and low spin iron atoms. In addition, opposite to others, the complex with Ni impurities presents a rotation of the principal axes.

Keywords: Spin transition compounds; First order reversal curves; Thermal hysteresis

1. Introduction

Due to elastic interactions, some of molecular magnets – the spin-transition solids – show a complex non-linear behavior including temperature, pressure, and light-induced thermal hysteresis (TH, PH and LITH). Considering the hypothesis that spin transition hysteresis involves like-spin domains, we applied in a systematic manner the Preisach-type approach derived from magnetism [1]. The sample is treated as an assembly of domains characterized by square-shaped hysteresis loops (the so-called hysterons) [2], the up- and down-switching values of which, T_{up}, T_{down}, are distributed. The result of a Preisach analysis is a bi-dimensional distribution of switching temperatures, $P(T_{up},T_{down})$, in the case of TH and LITH. In certain cases, the distributions could be directly linked with some physical properties of the material.

Among other several experimental strategies, the first order reversal curve (FORC) method allows a direct determination of the two-dimensional distribution, which is model-free but remains totally phenomenological. The FORCs are a specific class of minor hysteresis loops, for which the sweeping process of the input parameter is reversed only once.

The first FORC analysis of a spin transition was briefly reported in [3], and we have then presented in [4] a more extensive application of the method, aiming to describe the spin-like domain properties in terms of physical quantities such as the energy gap and the intra-domain interaction. The selection of these physical parameters, in turn, relies on the preliminary choice of a given model. Ours previous studies were performed in the frame of an Ising like model [5]. In a first approach the energy gap corresponds to the bias of the hysteresis loop and the interaction to its width (coercivity).

The macroscopic parameter used to characterize the state of the system is the high spin fraction, n_{HS}, that is

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the ratio between the number of molecules in high spin state and the total number of molecules.

For a thermal transition the warming/cooling modes are to be distinguished and there are two different types of FORC experiments, according to the sense of the thermal variations. The measurements start at a sufficiently high/low temperature, such that the high/low temperature (HS/LS) domain structure is saturated. Then temperature is lowered/raised until a given temperature T_b/T_b^*, the reversal temperature, and afterwards raised/lowered, in the warming/cooling mode, respectively, as illustrated in Fig. 1. During the second step of the process, n_{HS}/n_{HS}^* is measured as a function of the actual temperature, T_a/T_a^*. The experiment is repeated for several values of T_b/T_b^*, and the set of $n_{HS}(T_a,T_b)/n_{HS}^*(T_a^*,T_b^*)$ values forms the FORC data.

The FORC distribution is defined as the second mixed derivative of these curves:

$$\rho(T_a,T_b) = -\frac{\partial^2 n_{HS}(T_a,T_b)}{\partial T_a \partial T_b}$$

In the case of non-interacting domains, the FORC distribution $\rho(T_a,T_b)$ is equivalent to the Preisach distribution, e.g. $P(T_{down},T_{up})$ in the warming mode and $P(T_{up},T_{down})$ in the cooling mode. In such a case, the FORC distributions obtained in the cooling and warming modes are expected to be the same, in the limit of inherent experimental errors [4].

Diluted systems are of higher interest for investigating the nature and range of interactions. In the mean-field description, the "effective" interaction in the diluted system is proportional to the number of spin-crossover neighbours, i.e., to the composition parameter x and qualitatively explains why the hysteresis loop collapses bellow a threshold value $x = 0.40$ in the isostructural systems $[Fe_xM_{1-x}(btr)_2(NCS)_2]\cdot H_2O$ where the dilution metal M was Co or Ni [6,7].

In the case of pure and diluted spin transition materials $[Fe_xZn_{1-x}(btr)_2(NCS)_2]\cdot H_2O$, we calculated distributions of internal stresses and domain size, increasing with dilution $(1-x)$. The FORC analysis shows, for increasing dilution parameter an increasing width of the bias distribution, a decreasing width of the coercivity distribution, as well as an increasing correlation between the bias and coercivity distribution. The large variation of the mean transition temperature upon the effect of dilution can be explained by the large ionic radius of the Zn(II) ion, which roughly matches the Fe(II) ion radius in the high spin state.

The representative major thermal hysteresis loops of some Ni diluted compounds are reported in Fig. 2. In Fig. 3, we present the spin state phase diagram for all the three dilutions. A threshold dilution value, which is the limit of the Fe concentration that implies the presence of a hysteresis can be established for every impurity, varying from 0.3 in the case of Zn to about 0.5 for Ni. The large variation of the threshold value, as of the mean transition temperature upon the effect of dilution can be explained by different ionic radius of the impurities. Following the steric arguments used in [6,7], the presence of molecular units with a large radius stabilizes the high spin state of the spin-crossover units, i.e. lowers the equilibrium temperature.

In this paper, we shall present a throughout experimental investigation using the FORC diagram for different dilution metals (Zn, Co and Ni).

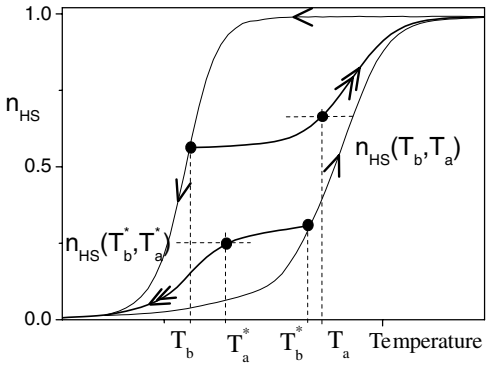

Fig. 1. A FORC in warming and cooling mode.

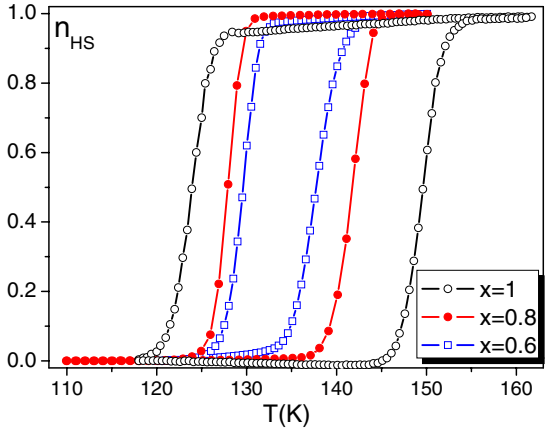

Fig. 2. Thermal hysteresis of $[Fe_xNi_{1-x}(btr)_2(NCS)_2]\cdot H_2O$ for different concentrations.

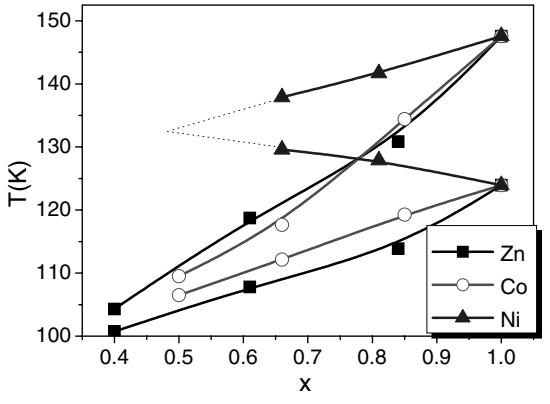

Fig. 3. The dilution phase diagrams of Fe $x = 1$, Zn ($x = 0.8$, 0.6 and 0.4) Co ($x = 0.8$, 0.6 and 0.5) and Ni ($x = 0.8$ and 0.6) taking the switching temperatures corresponding to $n_{HS} = 0.5$.