Study of the relaxation in diluted spin crossover molecular magnets in the framework of the mechano-elastic model

Cristian Enachescu,1,a) Laurentiu Stoleriu,1 Alexandru Stancu,1 and Andreas Hauser2

1Department of Physics, Alexandru Ioan Cuza University, 700506, Iasi, Romania
2Département de Chimie Physique, Université de Genève, CH-1211, Switzerland

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We model here the behavior of spin transition compounds, considering molecules arranged in a 2D hexagonal lattice and interacting via springs. The role of impurities in the clustering and nucleation phenomena is analyzed, as well as the manner in which the impurities affect the relaxation curves. The switching of the individual molecules is checked using a Monte Carlo procedure. When a molecule changes its state, it also modifies its volume, and the new equilibrium positions of all the molecules are calculated. As in previously reported experiments, it is found here that bigger impurities slow down the relaxation from the metastable high-spin state to the low-spin state, while smaller impurities act in an opposite way. It is shown that if the concentration of the impurities is higher than a certain threshold, then they act as a barrier, straitening the fast evolution of domains developing from the edges. © 2011 American Institute of Physics. [doi:10.1063/1.3556702]

The spin transition (ST) compounds are molecular magnets capable of switching between two states in thermodynamic competition: the diamagnetic low-spin (LS) state and the paramagnetic high-spin (HS) state, suitable for various applications such as recording media.1

The two states have different magnetic and optical properties, unit cell volumes (HS compounds are larger), and metal-ligand bond lengths. Due to thermodynamic considerations, the LS state is the stable state at cryogenic temperatures, but it can be transformed to the metastable HS state by irradiation with an appropriate wavelength—the so-called light induced excited spin state trapping (LIESST) effect.2 If the light is switched off, the HS state relaxes back to the stable LS state by way of a nonradiative process. In molecular solids, the differences between the volumes of HS and LS molecules are the source of elastic interactions that determine, if they are large enough, the sigmoidal, self-accelerated character of the HS-LS relaxation curve and its deviation from the first order kinetics. This phenomenon is called cooperativity, and it is usually modeled as a superposition of two components: a short-range interaction, depending on the shape and distance between neighbor molecules, and a long-range interaction proportional to the average number of HS molecules per unit volume.3–5 The evolution of the system is described here by the fraction of molecules in the HS state, denoted here as \( n_{\text{HS}} \).

A common method to clarify the role of these elastic interactions is based on the study of the metal ion dilution in the solid state. If the HS molecules are replaced progressively with neutral impurities, the spin transition molecules are more and more isolated, and, consequently, the HS-LS relaxation is more gradual, an indication of a progressive loss of cooperativity. The direct effects of dilution depend on the volume of impurities (bigger or smaller than that of the ST molecules in a HS state) and can be separated into two categories: (1) increase of the average distances between ST molecules, and (2) development of interactions between ST and impurity entities.6

In this paper, we use the recent mechano-elastic model7 to explain the influence of impurities on spin crossover complexes. We begin by presenting the key elements of the model, in which a single spring constant stands for both above-mentioned interaction types. We then proceed to a discussion of the results of the model, including a short comparison with similar attempts in the literature.

In the mechano-elastic model,7–9 the spin crossover molecules are represented as rigid spheres connected by springs, situated in a 2D hexagonal lattice. In the system without impurities and with all the molecules in the same state (i.e., HS state), all the springs are unstressed. The impurities can be introduced into the system by randomly replacing some of the spin transition molecules. In this case, the network is deformed, and its total area changes. If the volume of impurities is bigger than that of HS molecules, then the sample area increases (Fig. 1, top); conversely, with smaller volumes of impurities the sample area decreases (Fig. 1, bottom). The springs can then be elongated or compressed, depending on the position of every molecule and on the system configuration.

For the study of relaxation, in the initial state, all the ST molecules are HS. The probability of a molecule’s switching between HS and LS states depends on the individual local pressure \( p_i \), defined as the sum of pressures applied to that molecule by all neighboring springs, and on other parameters that are the same for all ST molecules: the activation energy \( E \), the temperature \( T \), and the factor \( k \) that establishes to which extent the local pressure influences the relaxation probability:7

\[
P_{\text{HS-LS}} = k_0 \exp \left( -\frac{E - kp_i}{T} \right).
\]
According to a Monte Carlo standard algorithm, we check the ST molecules in the system to verify whether they switch or not over the time studied. For every ST molecule, we compare the probability [Eq. (1)] with a random number \( g \in (0, 1) \). The molecule changes its state (and consequently its volume) only if this number is smaller than the probability. A Monte Carlo step is concluded when all molecules in the system have been verified once.

When a molecule changes its state, an instantaneous force will appear inside neighboring springs, resulting at first in a shift in the position of neighbor molecules and then, progressively, of all other molecules in the system. The motion of molecules stops when all of them are in mechanical equilibrium. In order to find the equilibrium positions for all molecules in the system after every Monte Carlo step, we consider that each molecule has a damped oscillatory-type motion; the equilibrium state is found, then, by solving a system of coupled differential equations for all molecules in the system, until the equilibrium is obtained (see Ref. 8 for details).

The cooperative effects in ST compounds can be efficiently modulated by replacing ST molecules (usually Fe) with neutral ones (such as Zn, Ni, or Co). From the experimental data (see, for example, Refs. 10–12), it is known that for the same STC concentration, the relaxation can be faster or slower as a function of the cation types used to substitute for ST molecules. For example, if an Fe molecule (92 pm in diameter) is replaced with a (bigger) Zn molecule (96 pm), the HS state is stabilized and the relaxation is slower, while in the case of (smaller) Ni impurities (83 pm) none of the states is favored.  

In Figure 2, we present relaxation curves simulated in the framework of the present model for various concentrations and sizes of impurities. As expected, the relaxation curves have the sigmoidal shape typical for a cooperative process, as the energy barrier progressively decreases while the relaxation proceeds. The relaxation is slowing down if the impurity volume exceeds that of HS ST molecules; conversely, the relaxation time increases for higher concentrations or bigger volumes of impurities. Also, the shape of the relaxation curves seems to be less sigmoidal if impurities are present in large numbers—as we shall see later, they create local barriers, slowing down the growth of clusters formed by freshly converted LS molecules.

In the mechano-elastic model, the cooperativity has been explained in terms of local pressure variation: when a molecule changes its state from HS to LS, the pressure acting on all other molecules in the system, and even on those situated at large distances, changes. Consequently, the local distortions cause effective long-range interactions among all molecules in the system. From the transition probability [Eq. (1)], it results that the local pressure influences the relaxation probability in such a way that a positive local pressure increases the HS relaxation rate. Opposite to the model without impurities—where, in the absence of external

In Figure 3, (Color online) Distribution of the local pressure for the HS molecules at the beginning of the relaxation for bigger (solid line) and smaller (dotted line) impurities.
pressure, the local pressure is zero in the whole system—if impurities are added, then the local pressure will be different in different nodes inside the sample. We represent in Fig. 3 the distribution of local pressures for dilution with bigger or smaller impurities. It can be noticed that in both cases, the distributions are close to Gaussian, but while for smaller impurities most of the local pressures are positive, for bigger impurities the average of the distribution is negative. This is consistent with the observations in Fig. 2: smaller volumes of impurities accelerate the relaxation, while larger volumes of impurities decelerate it.

The onset of correlation has been extensively studied, both theoretically and experimentally, for spin crossover complexes. It was first simulated using the Ising-like Hamiltonian, solved by the Monte Carlo Metropolis technique. Very recently, ball and spring models solved by molecular dynamics have reproduced the domain spreading inside the crystal, and optical microscopy experiments have offered a view of the spin crossover behavior at a molecular scale. However, studies of diluted spin crossover complexes are far less numerous. For example, in Ref. 4 it is stated that even a very moderate dilution of mixed crystals with the isostructural Zn-host suppresses the correlations; however, the authors do not present relevant images of the system during its evolution.

In Figure 4, we present snapshots corresponding to three diluted systems with different concentrations of impurities, taken during relaxation when around 20% of the initial HS state molecules had switched. The three systems have been studied using the same parameters and random number sequences. For the sake of simplicity, the impurity volume is considered here to be equal to that of HS molecules. For nondiluted systems (Fig. 4, top), the fast growth of a single cluster throughout the sample (starting from the edge) leads to fluctuations, nucleation, and growth phenomena. For a rather small concentration of impurities, one can identify several clusters of molecules in the same spin state developing at the same time. If the impurity concentration is higher than a certain threshold, then the evolution of the system is governed by a mean field regime, and no clusters are present. In this latter case, the impurities act as barriers, preventing the cluster development.

In this paper, we have studied the effect of impurities on spin transition compounds in the framework of the mechano-elastic model, and we have shown that most of the experimental features can be reproduced accurately by this model. We have also studied the influence of impurities on cluster and domain formation, and we have shown that there is a threshold value for the concentration that separates the avalanche and mean-field regimes. Further work will study the effect of impurities on the hysteretic behavior of spin transition compounds.

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References