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Influence of pressure and interactions strength on hysteretic behavior in two-dimensional polymeric spin crossover compounds

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ABSTRACT

A study of thermal behavior for two-dimensional spin-crossover compounds is performed by using an Ising-like model including both short-range and long-range interactions and a Monte Carlo entropic sampling technique for determining the associated density of states. The effects of various factors, such as external pressure, internal interaction strength or system size, on the thermal transition are analyzed and compared to several experimental findings in this area. The study is focused on two-step transitions and the conditions for hysteresis behavior at each step which are especially important for the potential applications of spin-crossover materials in data storage devices or smart sensors.

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1. Introduction

The design and fabrication of new spin crossover compounds (SCO), with potential applications in various spintronic and photonic devices (memories, sensors, displays) have attracted significant research interest over the last years [1–3]. Since significant changes in optical and electrical properties are observed in these compounds when switching from a low-spin (LS) state to a high-spin (HS) state [4,5], the main goal of this scientific area is to control these phase transitions induced by various external factors such as temperature, pressure, and light irradiation [6–8]. The most common LS–HS transition induced by temperature has one-step shape, that can be gradual, abrupt or with hysteresis [9,10]. Recently, two-step [11–13] and three-step [14–16] transitions with or without hysteresis loops have been reported. In this paper we consider a two-dimensional SCO system, $Fe(py)_2[Ag(CN)_2]_2$ (py=pyridine) compound [12], which displays a two-step transition with one hysteresis loop of 14 K width having the threshold temperatures at $T_{1/2}^{\uparrow}(1)=104$ K and $T_{1/2}^{\downarrow}(1)=90$ K [12]. The study of the two-step SCO transitions has been previously approached by considering two different sub-lattices or binuclear molecules [17–19]. Here, we show that such behavior can be explained in single lattice systems of mononuclear molecules as interplay between short-range and long-range interactions by taking into account the energy gap between the LS and HS states and their degeneracies. The influence of applied external pressure on transition shape is also examined based on the dependence of the energy gap on pressure.

By associating a pseudo spin σ to each molecule, with $\sigma=+1$ when the molecule is in HS state and $\sigma=-1$ when the molecule is in LS state, an Ising-type model can be constructed to describe the compound behavior. By considering that HS and LS states have degeneracies g_{HS} and g_{LS} while the difference between the two corresponding energy levels is Δ, the total energy of a system with N molecules can be described by the following temperature-dependent Hamiltonian [20]:

$$H=\left[\frac{\Delta}{2}-\frac{k_BT}{2}\ln\left(\frac{g_{HS}}{g_{LS}}\right)\right]\sum_{i=1}^{N}\sigma_i-J\sum_{\langle i,j\rangle}\sigma_i\sigma_j-G\sum_{i,j=1}^{N}\sigma_i\sigma_j \quad (1)$$

where k_B is Boltzmann's constant, J and G are accounting for the strength of short-range and long-range interactions between the molecules, respectively and the second sum is only taken over the nearest neighbors. By applying a mean field approach, this Hamiltonian can be written as

$$H=-h_f\sum_{i=1}^{N}\sigma_i-J\sum_{\langle i,j\rangle}\sigma_i\sigma_j, \quad (2)$$

where

$$h_f=-\left(\frac{\Delta-k_BT\ln(g_{HS}/g_{LS})}{2}-G\langle\sigma\rangle\right), \quad (3)$$

with $\langle\sigma\rangle$ being the average value of the fictitious spin. We aimed at computing the high-spin fraction of this system, $n_{HS}=(\langle\sigma\rangle+1)/2$, and at analyzing its temperature variation under the influence of various factors. The novelty of this Ising-like model is

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given by the consideration of long-range interactions and temperature-dependence in the Hamiltonian structure. The long-range interactions result from the elastic interactions between molecules and have been also taken into account in mechanoelastic [21–23] and atom-phonon coupling models [24–28], while the explicit temperature dependence appears from the consideration of state degeneracies.

2. Methodology

The exploration of state space associated to Hamiltonian (2)–(3) is limited to the most probable configurations in the standard Monte Carlo Metropolis algorithms. Although several generalizations have been proposed, they face serious difficulties in connecting separate pieces of information for a global description of state space. Here, we used a biased Monte Carlo (MC) technique [29–31,19] which favors the configurations belonging to low-degenerate macrostates and dampens those belonging to high-degenerate macrostates. Thus, a uniform exploration of state space is achieved and used to compute the density of states.

The total energy of the system (2)–(3) and the canonical partition function can be expressed in terms of two macroscopic variables: the total spin $m=\sum_{i=1:N}\sigma_i$ and nearest-neighbor correlations $s=\sum_{\langle i,j\rangle}\sigma_i\sigma_j$ as follows:

$$E(m,s)=-h_f m-Js \text{ and } Z_T=\sum_{m,s}D(m,s)\exp\left[-E(m,s)/k_BT\right] \quad (4)$$

where $D(m,s)$ is the number of configurations for a given set of macroscopic variables $\{m,s\}$, i.e. a discrete approximation of the density of states, and is the central part in determining the macroscopic thermodynamic quantities characterizing the system. For convenience, $D(m,s)$ will be termed as the density of states in the following. The process of determining $D(m,s)$ is run iteratively, where at each step i, a biased MC sampling with probabilities inversely proportional to $D_i(m,s)$ yields the histogram of the frequency of macrostates $H_i(m,s)$ and the subsequent density of states $D_{i+1}(m,s)=D_i(m,s)H_i(m,s)$. The initial density of states can be assumed uniform while the flat histogram can be considered as a convenient convergence criterion for this iterative process. As a result, the average spin value can be expressed as follows in terms of effective field h_f:

$$\langle\sigma\rangle=\frac{\sum_{m,s}\frac{m}{N}D(m,s)\exp[(h_f m+Js)/k_BT]}{\sum_{m,s}D(m,s)\exp[(h_f m+Js)/k_BT]} \quad (5)$$

By taking into account the linear relation (3) between the effective field h_f and $\langle\sigma\rangle$, a self-consistent equation for $\langle\sigma\rangle$ is thus obtained. Our analysis is performed by solving this equation and studying the variation of its solution with temperature T for various values of system parameters Δ, $J(<0)$, $G(>0)$, and N.

The influence of pressure on the transition shape is analyzed through the linear dependence of the energy gap Δ on the pressure p, $\Delta=\Delta_{ap}+\alpha p$, where Δ_{ap} is the energy gap at ambient pressure, α is the difference of the volumes corresponding to the pressure p and to the ambient pressure.

3. Results and discussions

By using the Ising-like model and the MC entropic sampling method presented above, we study the thermal hysteretic behavior of a two-dimensional SCO system. In order to set the framework for our analysis, we assumed the degeneracy ratio $\ln(g_{HS}/g_{LS})=\Delta S/R=4.6$ and the energy gap $\Delta=\Delta H/R=582.15$ K, where the enthalpy change ΔH and the entropy change ΔS were taken from the experiments performed in [12] on $Fe(py)_2[Ag(CN)_2]_2$ compound, while R is perfect gas constant.

The long-range interaction strength was first fixed to 360 K while the short-range interaction strength was varied between −100 K and −20 K. Selected representative results obtained in these simulations are presented in Fig. 1. For strong local antiferromagnetic-type coupling ($J=-80$ K) a hysteretic half-transition is observed at low temperature followed by a gradual transition to HS state at high temperature. The intermediate plateau connecting the two behaviors (corresponding to $n_{HS}\sim0.5$) is narrowed down with the decrease of $|J|$ until vanishes and a full hysteretic transition is observed (see, as an example, the curve corresponding to $J=-30$ K). Let us notice that the thermal behavior corresponding to $J=-68$ K is similar to the one experimentally observed in [12] with a high temperature step occurring around 150 K and a low temperature hysteretic transition of 14 K width occurring around 90 K. In a second study, the short-range interaction strength was fixed to this value ($J=-68$ K) while the long-range interaction strength was varied between 200 K and 600 K. Selected representative results obtained in these simulations are presented in Fig. 2. For weak long-range ferromagnetic-type interactions, a two-step gradual transition is observed (see the curve corresponding to $G=200$ K). The increase in interaction strength leads first to the formation of a hysteretic transition in the low temperature region and to a narrower intermediate plateau ($G=360$ K). Further increase in the long-range coupling leads a second hysteretic transition in the high temperature region ($G=430$ K). Finally, the thermal behavior of strongly coupled compounds features a full hysteretic transition, while some intermediate metastable states might still exist but they are not achievable by temperature variation ($G=530$ K); however these intermediate metastable states might be attained by different external factors such as light irradiation of pressure.

The previous analysis was performed for a system with 64 molecules. The thermal behaviors for systems with different sizes were also analyzed and the results obtained for the size of 16 and 144 molecules are presented in Fig. 3. While the qualitative features are similar to the ones previously observed for $N=64$, several quantitative differences are noticeable. When the system size is increased, the low hysteretic loop widens and moves to lower temperatures while the high gradual transition moves to higher temperature and becomes smoother. These two effects are contributing to a larger intermediate plateau when the system size is increased.

The last part of our study is dedicated to the influence of external pressure on the thermal behavior of SCO compounds. In Fig. 4 it is shown that all three types of two-steps transitions

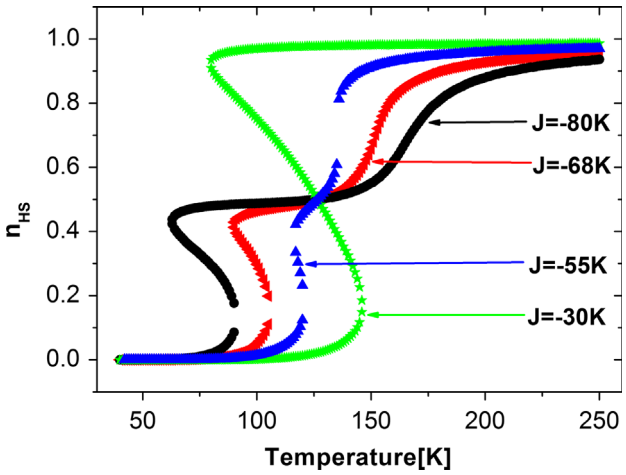

Fig. 1. Dependence of HS fraction- n_{HS} on temperature for different short-range interactions (J) strength. The values of the other system parameters are: $\ln(g_{HS}/g_{LS})=4.6$, $\Delta=582.15$ K, $G=360$ K, and $N=64$ molecules.