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Role of the impurities in 2D spin crossover nanoparticle: Monte Carlo study

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This work is devoted to the study of the impurities effect in 2D spin crossover nanosystem in frame work of an Ising-like model. Results were obtained by means of Monte Carlo modeling technique, based on the heat bath algorithm. It is shown, that the impurities change the system's thermal hysteresis width and shift the spin transition curves (HS → LS). In this manner, impurities can act as an additional influence parameter on the transition curves. The considered effect is not significant, but nevertheless should be taken into account in the developing process of nanoscale devices based on spin crossover compounds.

Keywords: spin crossover, Ising-like model, Monte Carlo method, spin transition, thermal hysteresis.

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Introduction

Spin-crossover compounds are bi-stable molecular magnetic complexes (functional switching materials) that are able to change their physical properties under the actions of different external factors, such as temperature, pressure, light irradiation, magnetic field, etc. The electronic configuration of such transition metal ions (Fe^{2+}, Fe^{3+} and others) have one of two stable states: low-spin (LS) state and high-spin (HS) state. The main feature of spin-crossover materials lies in the possibility to control the switching process between mentioned states. Due to the elastic interactions between their molecules they exhibit non-linear behavior including temperature, pressure and light induced thermal hysteresis [1-3].

Nanoscale spin-crossover materials are good candidates for various types of practical applications [4-6]. They can be used as active materials for data storage and processing devices, temperature or pressure sensors, etc. For instance, the possibility of producing spin-crossover memory storage devices with a size of 4 nm^3 of elementary cell was shown by Kahn and Martinez [7]. Later by Matsumoto and others [8] there was reported about a programming possibility of spin-state switching process in a mixed-valence spin-crossover grid. The spin states of metal ions were selectively switched due to the use of laser stimulation allowing the spin-crossover molecules to exist in three different discrete levels (phases). The successful synthesis of 1D chain and 2D spin-crossover network structure has been reported by Gao and others in the work [9]. In which, the property of a reversible color change at room temperature under the pressure action has demonstrated that they are good candidates as a basic material for pressure sensors.

One of the essential problems on a nanoscale level is the study of the impurities impact. In other words, the investigation of the impurities influences the nanosystem properties. Concerning spin-crossover materials, this issue has been investigated in many works. For instance, the study of the dilution effect in spin-crossover compound diluted on a high-spin cobalt (II) matrix [10]. Investigation

of impurities effect in spin-crossover material based on FORC (first order reversal curves) method [11]. The study of the impurities impact on the clustering and relaxation phenomena in spin-crossover compound in framework of an mechano-elastic model [12] and the like.

The article is an attempt to complement the above mentioned works and to expand the existing theoretical knowledge concerning spin-crossover compounds. More detailed description of the obtained results is given in the following sections.

I. Theoretical model and simulation technique

There are many theoretical description models of spin-crossover materials. But in general, they all can be divided into two main groups. Macroscopic [13, 14] and microscopic [15, 16] models. This study was conducted within the framework of microscopic Ising-like model. It is worth mentioning, that similar approach was successfully used to investigate the properties of the $[Fe(Fpz)_2Pt(CN)_4]$ spin crossover compound under the action of external pressure [17]. Where the obtained theoretical results are in complete accordance with the experimental ones. The Hamiltonian of the considered phenomenological, microscopic Ising-like model takes the following form:

$$H = -J_1 \sum_{<i,j>} s_i s_j - J_2 \sum_{<i,j>} \sigma_i \sigma_j - J_3 \sum_{<i,j>} s_i \sigma_j - h(\sum_i s_i + \sum_j \sigma_j), \quad (1)$$

here s_i and σ_i are the pseudospin variables (i = 1, 2, …, N) of the spin crossover molecules (nodes) of the main lattice and impurities, respectively. They take following values s_i = σ_i = ± 1, which corresponds to HS and LS state respectively. <i, j> denotes the interaction between the nearest (neighboring) spin nodes. As it follows, the inter-molecular interaction is considered in the nearest neighbor approach. It is known, that the impurities present in a material can cause and simultaneously influence different effects. In this approach, we consider the impurities influence on the system's parameters only in context of the exchange interaction. Thereby, J_1 is the exchange coupling between main lattice nodes, J_2 is the exchange coupling between impurities nodes, and J_3 is the exchange coupling between the main lattice nodes and impurities. J_1, J_2, and J_3 are positive (> 0) and correspond to ferromagnetic type of interaction (↑↑). More detailed schematic representation of the above mentioned inter-layer molecular interactions is depicted in fig. 1. Where squares represent the main lattice nodes and circles – impurities. Throughout the calculations $J_2 = J_1 \pm ½ \times J_1$ and $J_3 = (J_1 + J_2)/2$. Two possible cases where considered: $J_1 > J_2$ and $J_1 < J_2$.

In the Hamiltonian (1) h denotes the transition metal ion external field.

$$h = -\frac{1}{2}(\Delta - k_B T ln(g) + p\Delta V), \quad (2)$$

here Δ is the energy difference between LS and HS states (ligand field splitting energy), k_B is the Boltzmann constant (k_B = 1), T is the absolute temperature (in Kelvin's degree), g is the degeneracy ratio between LS and HS states, p is the external pressure and ΔV – the molecular volume change (after the spin transition is complete).

The simulation process was conducted within the framework of Monte Carlo method based on the heat bath algorithm, which uses the standard single spin-flip technique [18]. The transition probability for each spin is defined as:

$$P(s_i \to -s_i) = min[1, \frac{1}{\exp(\frac{\Delta H\{s_i\}}{k_B T})+1}], \quad (3)$$

where $\Delta H\{s_i\}$ is the energy difference between LS and HS states (before and after spin transition).

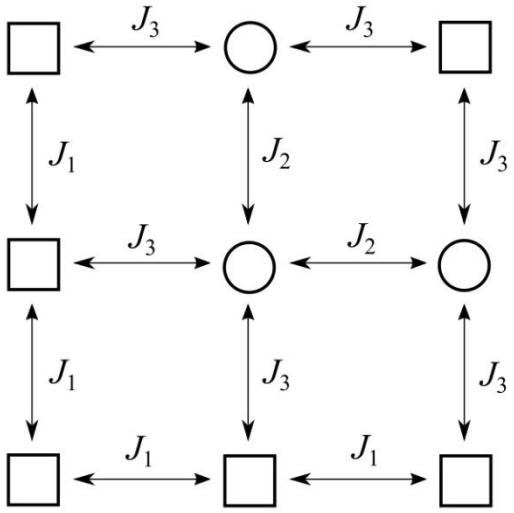

Fig. 1. Schematic representation of the inter-molecular interactions (J_1, J_2, and J_3) described by the Hamiltonian (1). Squares correspond to the main lattice nodes, circles – to the impurities.

The modeling was carried out on a 2D square lattice defined as $N = L \times L$ with free boundary conditions. Here L is the lattice side length and N is the number of nodes. A lattice with the size of 70 × 70 nodes was chosen, which is enough to eliminate the size effect [19]. To obtain reliable data of the systems evolution, 3000 Monte Carlo steps (N_{MC}) per Kelvin degree where used.

For each point (Kelvin degree), the system's magnetization m was found as:

$$m = \frac{\langle s \rangle}{N_{MC}} \quad (4)$$

where

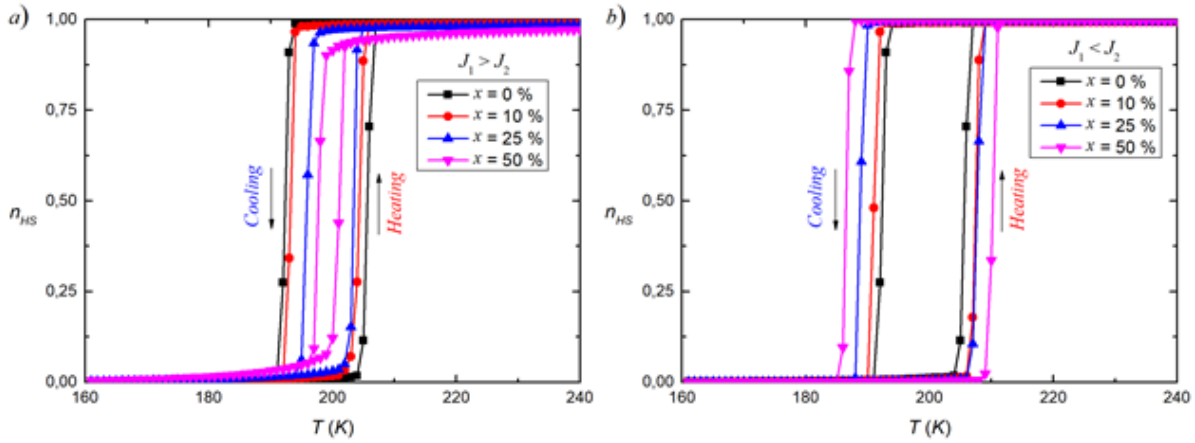

Fig. 2. Dependence of the HS fraction of molecules (n_{HS}) on temperature for different values of the impurities (x = 10%; 25%; 50%), a – the case for $J_1 > J_2$, b – $J_1 < J_2$ ($p\Delta V = 0$).

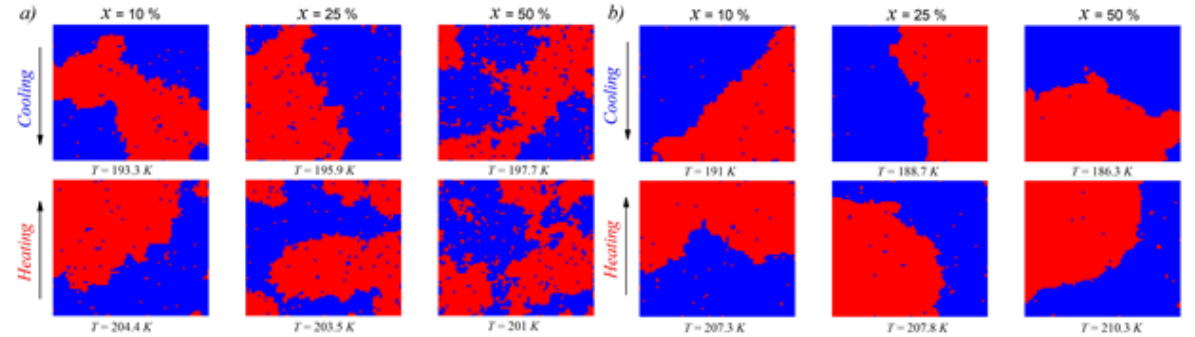

Fig. 3. Snapshots of systems evolution during spin transition for the value of n_{HS} = 0.5, and x = 10%; 25%; 50%, a – the case for $J_1 > J_2$, b – $J_1 < J_2$ ($p\Delta V = 0$).

$$\langle s \rangle = \frac{1}{N}\sum_i s_i. \qquad (5)$$

Due to the fact, that described above simulation process of the Hamiltonian (1) cannot directly describe the behavior of the system's order parameter (the fraction of molecules that are in HS state – n_{HS}), the next relation between magnetization and the system's order parameter was used:

$$n_{HS} = \frac{m+1}{2} \qquad (6)$$

For the simulation the following system's parameters were used: J_1 = 130 K, Δ = 1000 K, g = 150, $p\Delta V$ = [0, 400 K]. Above mentioned system parameters do not correspond to a specific spin crossover compound but allow one to obtain typical transition curves between LS and HS states for such materials (thermal hysteresis). The description of the obtained results is given in the next section.

II. Results and discussions

First, we investigated the impact of impurities on system's thermal hysteresis. Impurities were generated throughout the lattice according to the uniform distribution. Parameter x denotes the number of lattice impurities in a percentage ratio. Corresponding results are plotted in fig. 2. Vertical lines (↑ and ↓) in fig. 2 denote the heating and cooling branches respectively. As one can see from fig. 2, two situations are observed. In the first case (fig. 2a) a narrowing of the thermal hysteresis is present. In the second case (fig. 2b) – the expanse of the thermal hysteresis. Moreover, the amount of narrowing/expansion is directly related to the amount of impurities x present in the lattice. That is, the greater the amount of impurities, the greater the effect. This is, due to the fact, that the thermal hysteresis width (ΔT_C) strongly depends on J (exchange interaction constant) in spin crossover nanosystems [20].

In the first case (fig. 2a) $J_1 > J_2$ and $J_1 > J_3$, general exchange interaction constant of the system (J) decrease and so the hysteresis width. In the second case (fig. 2b) $J_1 < J_2$ and $J_1 < J_3$, J vice verse increases simultaneously with the hysteresis width. The bigger the values of impurities x (inserts of fig. 2), the correspondingly smaller (in the first case) or larger (in the second case) is the value of J and the hysteresis width respectively.

To obtain more detailed information about systems evolution during the spin transition (LS ↔ HS) the use of snapshots are required. Corresponding results are plotted in fig. 3. Given snapshots complement the above considered results. Data depicted in fig. 3 are obtained for the value of n_{HS} = 0.5 and different values of x and temperature (see captions). From fig. 3 one can notice that there is a difference between the considered cases (fig. 3a, 3b). Namely in the first case (fig. 3a) one can observe a formation of a slightly larger number of domains region of LS and HS states in comparison to the second case (fig. 3b) when x increases. This is due to the fact that in

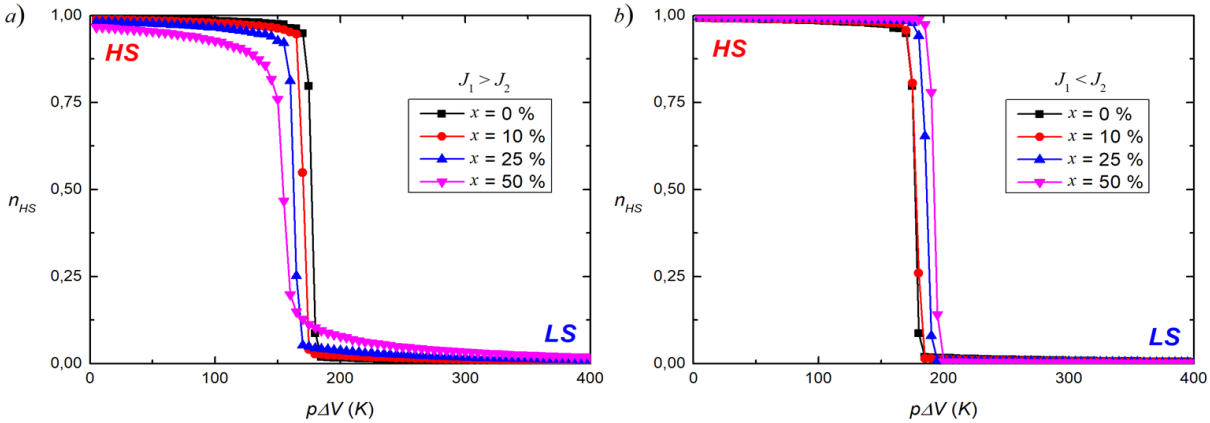

Fig. 4. Dependence of the HS fraction of molecules (n_{HS}) on pressure ($p\Delta V$) for fixed value of temperature (T=20 K), *a* – the case for $J_1 > J_2$, *b* – $J_1 < J_2$.

the first case ($J_1 > J_2$) the general value of the exchange coupling between spin crossover molecules of the system is smaller compared to the second case ($J_1<J_2$). As follows, the number of domains increases in the first case (fig. 3a) in comparison to the second one (fig. 3b) when *x* increases.

At last, the impurities influence on a transition type HS → LS for a fixed value of temperature (T = 220 K), was investigated. The corresponded results are given in fig. 4.

Due to the fact, that spin crossover material is very perspective compounds for new generation temperature and pressure sensors [21-23], investigation of the given case is very important. Note, that we are considering a case in which the thermal spin transition (LS → HS) is already completed (T = 220 K). As one can observe from fig. 4, there is a minor shift of the transition curves toward lower values of pressure ($p\Delta V$) for a case of $J_1 > J_2$ (fig. 4a) and toward larger values for the case of $J_1 < J_2$ (fig. 4b). The larger the values of the impurities (inserts of fig. 4), the larger the shift. In this situation, impurities can also serve as an additional influence parameter on the spin transitions. The effect is not significant, but nevertheless should be taken into account in the developing process of the pressure/temperature sensors based on spin crossover compounds.

It is worth mentioning, that the above discussed results are in accordance with the results of the similar works in this field of study [24, 25]. Also, they represent a logical continuation of works [26, 27].

Conclusions

The influence of the of the impurities on 2D spin crossover nanoparticle was investigated within the framework of an Ising-like model with the means of Monte Carlo simulation technique (based on the heat bath algorithm). The amount of the impurities can decrease/increase the system's thermal hysteresis, depending on the decrease/increase of the general exchange interaction *J*. In the case when the thermal spin transition has already taken place (for a fixed value of temperature) and with the help of pressure the reverse transition (HS → LS) is carried out, the influence of impurities leads to the shift of the transition curves. Therefore, impurities can be considered as an additional influence parameter on the transition curves. This shift is not noticeable, but should be taken into account in the developing process of different types of nanodevices, i.e. sensors (temperature, pressure).

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Роль домішок у 2D спін-кросовер наночастинці: Дослід Монте-Карло

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Ця робота присвячена дослідженню впливу домішок на 2D спін-кросовер наносистему в рамках моделі Ізінга. Результати отримані за допомогою методу моделювання Монте-Карло на базі алгоритму теплової ванни. Показано, що присутність домішок впливає на ширину теплового гістерезису системи та зміщує криві спінових переходів (HS → LS). Таким чином, показано, що домішки можуть виступати в якості додаткового параметру впливу на криві спінового переходу в таких системах. Розглянутий ефект не є суттєвим, але має місце, і тому його слід враховувати при розробці нанорозмірних пристроїв на основі спін-кросовер сполук.

Ключові слова: спін-кросовер, модель Ізінга, метод Монте-Карло, спіновий перехід, тепловий гістерезис.