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Role of reduced geometry on critical spin-crossover behavior in molecular magnet: Monte Carlo simulation

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ABSTRACT

In this work, the magnetic spin-crossover (SC) behavior was investigated using Monte Carlo simulation. The investigated SC structures were hexagonal films where each molecular magnetic spin was represented by the Ising spins interacting with neighboring spins with short-ranged exchange-type interaction and long-ranged mechano-elastic interaction. The SC spins were mobile but under spring-type interaction constraint. Monte Carlo simulation was used to attain the system mechanical equilibrium, and used to update spin configurations via the modified Wolff algorithm. With varying the films thickness, the radius ratio of the high-spin-state to the low-spin-state, and the system temperature, the thermal equilibrium magnetization was measured to extract the magnetic profiles as well as the fourth order cumulant of the magnetization. The critical temperature T_c was extracted via the cumulant-crossing extrapolated to the thermodynamic limit. From the simulation, the magnetization and magnetic susceptibility profiles were obtained as functions of temperature for films thickness ranging from one to four layers. The results show that with increasing films thickness the critical temperature increases due to stronger average short-ranged magnetic interaction. In addition, the greater radius ratio of the high-spin-state to the low-spin-state enhances the phase transition point since higher thermal energy level is required to compensate the larger thermodynamic work required by the volume changed. These results are in agreement with previous studies. The scaling relationship among the critical point, the radius ratio, and films thickness was also successfully proposed. With good statistical accuracy, this scaling formalism can then be used as qualitative guidelines to predict magnetic critical behaviors for further enhanced investigation or for designing desired functional SC applications.

1. Introduction

With the blossom of high-speed internet, gigantic digital data can be transferred across the world within seconds. This inspires development of digital recording storages for the transferred data. However, to continue increasing storage capacity, one needs to keep on reducing magnetic grain size, whereas at some points the grain may lose magnetic stability due to the 'superparamagnetic' effect [1,2]. Novel materials which can provide two stable discrete states at molecular-scale are thus in great demand. One promising material is spin-crossover (SC) solid [3], which is a type of molecular magnet containing transition metals surrounded by ligands [4,5]. In the SC materials, the SC molecules can exist either in the high-spin-state (HS) or in the low-spin-state (LS). The transition between these two states involves absorbing or releasing of the energy. In general, factors that induce or contribute state switching as well as the switching rate are temperature [6], light irradiation [7], magnetic field [8], pressure [9], etc. For instance, by applying appropriate heat or electromagnetic energy (e.g. light), LS can shift to HS, and later relaxes back when the supplied energy is turned off. One can therefore tune the relevant perturbation to obtain desired magnetic properties if SC transitioning process is fully understood. However, the SC material is very complex in its behavior. For instance, not only the magnetic spin interaction but also the spring-type interaction is crucial as the SC elastic volume depends on the fraction of the HS and LS molecules [10]. This is as the HS molecule is larger in size than that of the LS. This size mismatch then becomes the origin of intrinsic stress which later gives rise to an elastic volume change in lowering the system energy.

Typically, in modeling the SC materials, both short-ranged and long-ranged interactions are required. Nevertheless, the full understanding on the topic is still yet to complete. For instance, the combination between the short-ranged magnetic exchange interaction and the long-ranged mean-field type interaction were used to investigate the SC system and found to be able to reveal several spin-crossover characteristics such as the change of the thermal

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hysteresis with changing intermolecular interactions [11] and the enhance of the critical temperature with increasing external pressure [12]. However, the mean-field is known to overestimate the critical point in magnetic materials as important thermal fluctuation is discarded. Therefore, the accuracy of the results obtained is somewhat quantitatively in doubt. Further, this model seems to be lacking of physical explanation as it does not explain how spin-switching spreads throughout the whole system and how the spreading affects the overall magnetic properties. Therefore, other models which allow the view of this picture, such as the Monte Carlo (MC) simulation should be considered as an alternative. Recently, with the MC, there were attempts to tackle the SC problem by considering the long-ranged interaction where all the SC spins are coupled to their neighboring via harmonic potential [13], i.e. the elastic spring-type interaction [14–22]. Recent investigations include the study of clusters of state-switching percolation and associated volume change [14–18], the photoexcitation rate effect [15], the spin dilution effect [17], the finite spin-cluster effect [19–22], the size differences between spin-state volume effect [20], the external pressure effect [19,22], and effect of elastic interaction magnitude [15,19,22] on SC properties. Nevertheless, for the sake of simplicities, most theoretical studies simplified the SC system into monolayer structure [13–20] or into the bulk form [13,21,22]. However, in real magnetic recording application, SC substances are deposited as films on the substrate. Further, due to the structural non-uniformities, the propagation of intrinsic stress, induced by the size mismatches between the HS and LS molecules throughout the system is restricted due to the reduced geometries and films surface effect. Since the stress and its distribution are known to have strong effect on spin transition [19,22], the molecular magnetic behavior in films structure should be very different from the ideal two-dimensional and bulk cases, and the thickness dependence of the behavior is expected, such as the enhancement of the critical temperature and magnetic stabilities with increasing films thickness in ferromagnetic films [23–25].

Therefore, it is the objective of this study to model such a situation to provide another enhanced understanding of molecular magnetic materials under geometric restriction for various sizes of the SC molecules. The stochastic MC simulation was used to investigate how the random thermal exchanging between system and environment plays its part on spin configurations. The Ising model (with mechano-elastic interaction included) was considered where each Ising spins used represent SC molecular state, i.e.+1 (HS) and −1 (LS). The SC molecules were mobile interacting with neighboring spins via spring-type interaction [13–17,19,20,22]. The SC magnetic profiles were investigated though magnetization and magnetic susceptibility, while the critical temperature was extracted from the Binder's fourth order cumulant of the magnetization and finite size scaling analysis [13,20,26,27]. In the next section, important background theories and methodologies of how to use Monte Carlo simulation in this study is given. After that, the simulation results along with their explanation and discussion, accompanied by suggestion on how to advance the topic to the next level, are given in the results and discussion section. Finally, all the important results and key findings are summarized and given in the conclusion section.

2. Background theories and methodologies

The spin-crossover (SC) phenomena belongs to molecular magnet which the magnetic spins can exhibit at least two discrete states such as the diamagnetic low-spin-state (LS) and the paramagnetic high-spin-state (HS). These states are switchable under thermodynamic, electromagnetic, and mechanical competitions. On one hand, with applying electromagnetic energy, the LS can switch to HS if the provided energy is larger than the energy difference between HS and LS states (e.g. see Fig. 1). On the other hand, the HS could be promoted from the increase in temperature, due to the descent in the chemical potential [28] i.e. $-k_BT\log g$ where $g=\frac{g_{HS}}{g_{LS}}$ is the ratio of degeneracies of the HS to LS. The spring-like mechanical energy also plays its role in SC behavior. For instance, it induces the cooperative effect, i.e. the effect that temperatures at where number of HS and LS become equal are different depending on either cooling or heating history. With these behaviors, the SC Hamiltonian can be termed using the short-ranged Wajnflasz-Pick interaction [29] and the long-ranged elastic interaction as

$$H = H_{Is} + H_{LS,HS} + H_{Elas}. \tag{1}$$

In Eq. (1), the first term on the right hand side i.e. $H_{Is}=-\sum_{\langle ij\rangle}J_{ij}s_is_j$ is the Ising Hamiltonian, where $s_i=\pm1$ representing HS (+1) or LS (−1) states of the ith molecular magnet, J_{ij} is the short-ranged magnetic exchange interaction between spins at sites i and j, and the notation $\langle ij\rangle$ indicates that the sum includes only nearest neighboring pairs. In this work, the exchange interaction J_{ij} was assumed directional independent i.e. $J_{ij}=J$ and used as unit of energy (i.e. $J=1$). This then redefines unit of temperature as J/k_B and units of all energy terms as J, where k_B is the Boltzmann's constant. Next, the second term in Eq. (1) is according to the difference in the energy and chemical potential between states i.e. $H_{LS,HS}=\frac{1}{2}\sum_i(D-k_BT\log g)s_i$, where D is the energy difference between LS and HS. The last term in Eq. (1) is associated to the mechano-elastic energy between pairs of neighboring spins i.e. $H_{Elas}=\frac{1}{2}k_{sp}\sum_{\langle ij\rangle}\left(|\vec{r}_i-\vec{r}_j|-\left[R_i(s_i)+R_j(s_j)\right]\right)^2$ [13,20,22], where k_{sp} is an effective spring constant controlling the elastic interaction magnitude among spins, $\vec{r}$ is a spin position vector, and the molecular magnet radius $R_i=R_i(s_i)$ is a function of the spin-state which can assume only two discrete values depending on the spin s_i i.e. $R_i=R_{HS}$ for high-spin-state ($s_i=+1$) or $R_i=R_{LS}$ for low-spin-state ($s_i=-1$). Therefore, the molecular magnetic spin Hamiltonian Eq. (1) can be rewritten as

$$H=-\sum_{\langle ij\rangle}J_{ij}s_is_j+\frac{1}{2}\sum_i\left(D-kT\log g\right)s_i + \frac{1}{2}k_{sp}\sum_{\langle ij\rangle}\left(|\vec{r}_i-\vec{r}_j|-\left[R_i(s_i)+R_j(s_j)\right]\right)^2. \tag{2}$$

In this work, the main investigation was paid onto the films structure, the size of the molecular magnetic radius, and critical properties relation. Therefore, the simple case where $D=0$ and $g=1$ was considered [20] to stress out the SC critical temperature (T_c) where number of HS and LS become equal without interferences from state degeneracies and the energy differences between states.

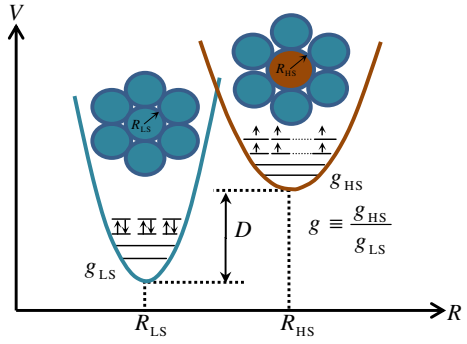

Fig. 1. Schematic diagram showing the potential dependence on magnetic molecular radius in typical SC materials.