Monte Carlo simulation of pressure-induced phase transitions in spin-crossover materials

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Pressure-induced phase transitions of spin-crossover materials were simulated by a Monte Carlo simulation in the constant pressure ensemble for the first time. Here, as the origin of the cooperative interaction, we adopt elastic interaction among the distortions of the lattice due to the difference of the molecular sizes in different spin states, i.e., the high spin (HS) state and the low spin (LS) state. We studied how the temperature dependence of the ordering process changes with the pressure, and we obtained a standard sequence of temperature dependences that has been found in changing other parameters such as strength of the ligand field (S. Miyashita et al., Prog. Theor. Phys. 114, 719 (2005)). Various effects of pressure on the spin-crossover ordering process are examined from a unified point of view.

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Several spin-crossover (SC) compounds have been extensively investigated [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20], and various theoretical analyses of the SC transitions have been reported [11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. In the SC compounds, a metal ion can be in either a low-spin (LS) or high-spin (HS) state, depending on the strength of the ligand field. Control of the spin state of SC compounds has been realized by applying external stimuli such as temperature, light-irradiation [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20], magnetic field [21, 22, 23, 24], and pressure [25, 26, 27, 28, 29, 30]. It has been pointed out that cooperative interactions play an important role for the SC transitions. With such interactions, various types of SC transition are realized, e.g., a smooth crossover or discontinuous first-order phase transition. For modeling of the interaction mechanism, a model with an Ising-type short-range interaction, e.g., the Wajnflasz-Pick (WP) model, has been proposed, and various aspects of cooperative behavior have been successfully explained [11, 12, 13, 14, 15, 16, 17, 18].

As the ligand field is changed, SC transitions show a standard sequence of temperature dependences of HS fraction \( f_{ HS}(T) \): (I) a smooth transition, (II) hysteresis, (III) hysteresis with a low-temperature metastable HS phase, and (IV) a HS phase stable at all temperatures. We found that this sequence also appears with changing degeneracy or strength of the interaction [17, 18]. Thus we call this the generic sequence. However, the origin of the interaction was not clear. Recently, it has been pointed out that the elastic interaction between distortions of the lattice due to the molecular size difference between the HS and LS states can induce phase transitions of the spin state [19]. In order to study the elastic interaction, besides the spin state, the positions of the molecules must be treated as dynamical variables to be equilibrated. This degree of freedom causes a change of the system volume. Therefore, the pressure \( P \) becomes an important parameter for describing the system. Thus, we are now at a stage where we can study the pressure effect by direct numerical study. In a previous study [19], we demonstrated that the elastic interaction can cause a spin transition in a 2D system with an open boundary condition. In this study, we adopt a similar elastic model in 3D. Although intramolecular potentials were taken into account besides intermolecular potentials in Ref. [19], in the present study we take into account two levels (LS and HS) with two different molecular sizes as the molecular state for simplicity. Here we adopt a method for the constant pressure ensemble in a periodic boundary condition. Moreover, we adopt a Monte Carlo (MC) method where we can easily control the degeneracy of the spin state. By this method, we succeeded for the first time in demonstrating pressure-induced phase transitions in a spin-crossover system.

The pressure effect has been one of the most important characteristics observed in SC compounds, and various interesting properties have been observed, e.g., a shift of the transition temperature, increase or decrease of hysteresis, stabilization of the LS state for the whole temperature region, and so on [25, 26, 27, 28, 29, 30]. To understand the pressure effects, a theoretical analysis based on each experimental phenomenon and the comprehensive theory of the free energy of the mean-field model has been reported [12, 13, 14, 15, 16, 17, 18]. In the present work, we study these effects by a direct numerical method, adopting a microscopic Hamiltonian and demonstrating the fundamental aspects in a unified microscopic picture.

We performed MC simulation on the simple cubic lattice. In the spin-crossover materials, the molecule at a
lattice point may be in the HS or LS state. We express the spin state at the \( i \)-th site by \( n_i \), which equals 0 for the LS state and 1 for the HS state. As important ingredients of the spin-crossover material, we set the energy difference of the state \( D(>0) \), and the degeneracies of the states: \( g_{\text{HS}} \) and \( g_{\text{LS}} \) for the HS and LS states, respectively. These properties are represented by the on-site Hamiltonian

\[
H_0 = D \sum_i n_i,
\]

(1)

In order to introduce interaction between spins, an Ising-like interaction \(- J \sum_{<ij>} n_i n_j \) was adopted in the WP model. Instead, we have attributed the interaction to the elastic interaction between lattice distortions caused by the difference of the molecular size between the HS or LS states. Therefore, we introduce the elastic interaction between the molecules:

\[
H = H_{nn} + H_{nnn} + H_0, \\
H_{nn} = \frac{k_1}{2} \sum_{\langle i,j \rangle} |r_{ij} - (R_i + R_j)|^2, \\
H_{nnn} = \frac{k_2}{2} \sum_{\langle\langle i,j \rangle\rangle} |r_{ij} - \sqrt{2}(R_i + R_j)|^2,
\]

(2) \quad (3) \quad (4)

where \( r_{ij} \) is the distance between the molecule on the \( i \)-th and \( j \)-th sites, and \( k_1 \) is the corresponding spring constant (Fig. 1). \( H_{nn} \) expresses elastic interaction between nearest-neighbor pairs \( (i,j) \). The interaction is a function of the molecular radius \( R_i = (1-n_i)R_{\text{LS}} + n_iR_{\text{HS}} \) of the \( i \)-th site, where \( R_{\text{HS}} \) and \( R_{\text{LS}} \) are the molecular radius of HS and LS states, respectively. We set the ratio of the radii to be \( R_{\text{HS}}/R_{\text{LS}} = 1.1 \). \( H_{nnn} \) expresses elastic interaction for next-nearest neighbor pairs \( (\langle i,j \rangle) \). In this study, we set the ratio of the spring constants, \( k_1/k_2 \), to be 10 [31].

For the simulation, we adopt the \( NPT-MC \) method [32] for the isothermal-isobaric ensemble with the number of molecules \( N \), the pressure of the system \( P \), and the temperature \( T \). The thermodynamic potential for the isothermal-isobaric ensemble is the enthalpy,

\[
H = E + PV,
\]

(5)

where \( E \) is the energy given by Eq. (1) and \( V \) is the volume of the system. The states of the system are specified by \( 4N+1 \) variables \((n_1, \ldots, n_N, r_1, \ldots, r_N, V)\). In the \( NPT-MC \) method, we have the following balance condition for the transition probabilities \( \{w_{i \rightarrow k}\} \):

\[
\frac{w_{i \rightarrow k}}{w_{k \rightarrow i}} = \exp(-\beta \Delta W),
\]

(6)

where

\[
\Delta W = (E_k - E_i) + P(V_k - V_i) - NT \log\left(\frac{V_k}{V_i}\right).
\]

(7)

The scheme of the simulation is as follows: (i) Choose a molecule randomly. (ii) Choose a candidate spin state \( n_i = 0 \) or 1 by the probability \( g_{\text{LS}}/(g_{\text{LS}} + g_{\text{HS}}) \) or \( g_{\text{HS}}/(g_{\text{LS}} + g_{\text{HS}}) \), respectively. (iii) Choose a candidate position of the molecule \( (r_i) \). Here, we use the scaled coordination length \( s = r_i/L \). The interaction is a function of the distance between \( i \) and \( j \) through the spring constant \( k_1 = 10k_2 \).

\[
\text{In Fig. 2 we depict } f_{\text{HS}}(T) \text{ for various values of } k_1 \text{ with } g(= g_{\text{HS}}/g_{\text{LS}}) = 20, D = 1, P = 0.01, \text{ and } k_1 = 10, 20, 30, 40, \text{ and } 50. \text{ When } k_1 \text{ is small, e.g., } k_1 = 10, \text{ the transition is gradual and hysteresis is observed. As } k_1 \text{ becomes large, the transition becomes sharp. For } k_1 = 40, \text{ hysteresis is observed between cooling and warming processes. Here, the transition temperature is } 0.28 \text{ for the cooling process and } 0.36 \text{ for the warming process. Snapshots of the spin configuration (a two-dimensional section of the lattice) are shown in Fig. 3. When } k_1 \text{ becomes larger, i.e., } k_1 = 50, \text{ the transition does not take place in the cooling process and the HS phase is maintained down to } T = 0. \text{ This observation indicates the existence of a HS metastable phase at } T = 0. \text{ The transition is gradual and hysteresis is observed.}
\]

FIG. 1: (Color online) Schematic illustration of the present model. HS/LS molecule consists of Fe atom (red/blue circle) and six ligands (gray circles).
In the warming process from low temperatures \cite{17, 18}. In the warming process from \( T = 0 \), the LS phase is transformed to the HS phase at \( T = 0.4 \).

We find that the change of \( k_1 \) causes a sequence of \( f_{\text{HS}}(T) \) that agrees with the generic sequence proposed in our previous papers. Thus, we expect that there is a case where a low-temperature HS metastable phase and thermal hysteresis are observed, which was found characteristic of this type of ordering processes and also was experimentally confirmed \cite{17, 18, 33}. In order to check the existence of the low-temperature HS metastable phase, we studied the warming-up process from HS from \( T = 0 \) for the system with \( k_1 = 40 \). The temperature dependence is depicted in Fig. 4 where the HS metastable phase exists and relaxes to the LS phase at \( T = 0.04 \). The LS phase changes to the HS phase at \( T = 0.36 \) as we saw in Fig. 2. Therefore, we find that the HS metastable phase and hysteresis are both observed. Now, we confirm that the present model realizes the generic sequence of \( f_{\text{HS}}(T) \) of the SC transitions.

Next, we study the pressure effect on the SC transitions. We study how \( f_{\text{HS}}(T) \) for \( k_1 = 50 \) changes when the pressure increases. In Fig. 5 we depict \( f_{\text{HS}}(T) \) during the warming process from the HS state. In the case of low pressure, \( P = 0.01 \), the transition is not observed, as shown in Fig. 2. When the pressure becomes \( P = 0.1 \), the initial HS state relaxes to the LS phase at \( T = 0.04 \), which indicates a low-temperature metastable HS state. Then, we find hysteresis with a jump at \( T = 0.32 \) in the cooling process and at \( T = 0.44 \) in the warming process. For \( P = 0.2 \), the initial HS state immediately relaxes to the LS phase, which indicates no low-temperature metastable HS state. Here, the hysteresis disappears and \( f_{\text{HS}}(T) \) is shifted to the high-temperature side. When the pressure increases further high, \( P = 0.5 \), the transition becomes gradual, and \( f_{\text{HS}}(T) \) is shifted to the high-temperature side. We define \( T_{1/2} \) at which \( f_{\text{HS}} = 1/2 \). In the hysteresis region we define it as \((1/2 - f_{\text{HS}})\) in the warming process is equal the \((f_{\text{HS}} - 1/2)\) in the cooling process. The pressure dependence of \( T_{1/2} \) is depicted in the inset of Fig. 5 which indicates that \( T_{1/2} \) increases linearly with the pressure.

We also study the pressure dependences of \( f_{\text{HS}}(T) \) at
various temperatures. In Fig. $f_{\text{HS}}(T)$ at $T = 0.3, 0.5$, and $0.7$ for $k_1 = 50$ are depicted as functions of the pressure. Here, the HS phase is set as the initial phase. At $T = 0.3$, a small pressure $P = 0.1$ induces the transition from the HS to the LS phases (red (i) arrow). The pressure-induced LS phase does not return to the HS phase in the process of reducing pressure (red (ii) arrow). This irreversible pressure effect indicates that the pressure stabilizes the LS phase and destabilizes the HS phase. At $T = 0.5$, the transition from the HS to the LS phase is observed at $P = 0.22$ during the pressure-increasing process (green (i) arrow). During the pressure-reducing process, the transition from the LS to the HS phases is observed at $P = 0.16$ (green (ii) arrow). That is, in this case we observe pressure-induced hysteresis. At $T = 0.7$, the transition between the HS and LS phases is smooth, and the hysteresis disappears. The present observations indicate that the pressure plays a similar role to that of the temperature for the SC transition.

The NPT-MC method for a three-dimensional system was established, and the effect of the pressure on the SC transition was studied. To our knowledge, this is the first attempt to study the pressure effect by direct numerical simulation, considering the local lattice distortions caused by the molecular size difference between HS and LS states in SC complex. In particular, we succeeded in observing a sequence of $f_{\text{HS}}(T)$ as a function of the pressure which agrees with that proposed as a general sequence the SC transitions.

In the present study, we kept the parameters $D$ and $g$ constant. If we take into account this pressure dependence, we can have a great variety of pressure dependences, which correspond to complicated dependences observed in experiments. For the next stage, we will study various pressure effects from the viewpoint of the present model and attempt to obtain a systematic understanding of the variety of pressure effects on the SC transitions.

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Phys. Lett. 101, 503 (1983).

[22] Y. Garcia, O. Kahn, J. P. Ader, A. Buzdin, Y. Meudesoif, and M. Guillot, Phys. Lett. A 271, 145 (2000).

[23] A. Bousseksaou, K. Boukeddaden, M. Goiran, C. Consejo, M. L. Boillot, and J. P. Tuchagues, Phys. Rev. B. 65, 172412 (2002).

[24] S. Kimura, Y. Narumi, K. Kindo, M. Nakano, and G. Matsubayashi, Phys. Rev. B 271, 145 (2000).

[25] A. Bousseksou, K. Boukheddaden, M. Goiran, C. Consejo, M. L. Boillot, and J. P. Tuchagues, Phys. Rev. B. 65, 172412 (2002).

[26] S. Kimura, Y. Narumi, K. Kindo, M. Nakano, and G. Matsubayashi, Phys. Rev. B 271, 145 (2000).

[27] S. Kimura, Y. Narumi, K. Kindo, M. Nakano, and G. Matsubayashi, Phys. Rev. B 72, 064448 (2005).

[28] S. Kimura, Y. Narumi, K. Kindo, M. Nakano, and G. Matsubayashi, Phys. Rev. B 72, 064448 (2005).

[29] J. Jeftic and A. Hauser, J. Phys. Chem. B 101, 10262 (1997).

[30] V. Niel, M. Muñoz, A. Gasper, A. Galet, G. Levchenko, and J. Real, Chem. Eur. J. 8, 2446 (2002).

[31] V. Niel, M. Muñoz, A. Gasper, A. Galet, G. Levchenko, and J. Real, Chem. Eur. J. 8, 2446 (2002).

[32] Y. Moritomo, M. Hanawa, Y. Ohishi, K. Kato, M. Takata, A. Kuriki, E. Nishibori, M. Sakata, S. Ohkoshi, H. Tokoro, and K. Hashimoto, Phys. Rev. B 68, 144106 (2003).

[33] Y. Moritomo, M. Hanawa, Y. Ohishi, K. Kato, M. Takata, A. Kuriki, E. Nishibori, M. Sakata, S. Ohkoshi, H. Tokoro, and K. Hashimoto, Phys. Rev. B 68, 144106 (2003).

[34] V. Ksenofontov, G. Levchenko, S. Reiman, P. Gültlich, A. Bleuzen, V. Escax, and M. Verdaguer, Phys. Rev. B 68, 024415 (2003).

[35] P. Gültlich, A. Gasper, V. Ksenofontov, and Y. Garcia, J. Phys: Condens. Matter 16, S1087 (2004).

[36] D. Papanikolaou, W. Kosaka, S. Margadonna, H. Kagi, S. Ohkoshi, and K. Prassides, J. Phys. Chem. C 111, 8086 (2007).

[37] The next-nearest neighbor interaction is introduced to maintain the cubic lattice, and the strength of $k_2$ is not important as long as the global shape of the lattice would not change.

[38] I. R. McDonald, Chem. Phys. Lett. 3, 241 (1969).

[39] H. Tokoro, S. Miyashita, K. Hashimoto, and S. Ohkoshi, Phys. Rev. B 73, 172415 (2006).