Monte Carlo Simulation of Pressure-Induced Phase Transitions in Spin-Crossover Materials

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Pressure-induced phase transitions of spin-crossover materials are studied in a microscopic model taking into account the elastic interaction among distortions of lattice due to the difference of the molecular sizes between the high-spin state and the low-spin state. We perform Monte Carlo simulations in the constant pressure ensemble and reproduce several important properties of the pressure effect in a unified way with a microscopic mechanism for the first time. The simulation newly reveals how the temperature dependence of the ordering process changes with the pressure.

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Several spin-crossover (SC) compounds have been extensively investigated [1–10], and various theoretical analyses of the SC transitions have been reported [11–23]. 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 [1–9,16,19], magnetic field [24–27], and pressure [28–34]. 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 a discontinuous first-order phase transition. For modeling of the interaction mechanism, models with an Ising-type short-range interaction, e.g., the Wajnflasz-Pick (WP) model, have been proposed, and various aspects of cooperative behavior have been successfully explained [11,14,16,20,21]. As the ligand field is changed, SC transitions show a sequence of temperature dependences of HS fraction $f_{\mathrm{HS}}(T)$: (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 [20,21]. 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 with the change of the system volume [22]. 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 the previous study [22], we demonstrated that the elastic interaction causes a spin transition in a 2D system with intra- and intermolecular potentials. In this study, we adopt an elastic model in 3D. 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.

It has been pointed out the importance of the effects of the pressure on SC compounds for their functional properties, 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 [28–34]. To understand these pressure effects, theoretical studies based on the free energy of the mean-field model have been reported [12,13,18]. 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. The molecule at the i-th lattice point is the HS or LS state, which is expressed by $n_i = 1$, or 0, respectively. We set the energy difference of the states $D(>0)$, and the degeneracies of the states: g_{HS} and g_{LS} for the HS and LS states, respectively. These properties are represented by the on-site Hamiltonian $\mathcal{H}_0 = D\sum_i n_i$. For the interaction between spins, an Ising-like interaction $-J\sum_{\langle ij\rangle} n_i n_j$ was adopted in the WP model. Instead, we have attributed the interaction to the elastic interaction between lattice distortions. Therefore, we introduce the elastic interaction between the molecules:

$$\mathcal{H} = \mathcal{H}_{nn} + \mathcal{H}_{nnn} + H_0, \tag{1}$$

$$\mathcal{H}_{nn} = \frac{k_1}{2}\sum_{\langle i,j\rangle}[r_{ij} - (R_i + R_j)]^2, \tag{2}$$

$$\mathcal{H}_{nnn} = \frac{k_2}{2}\sum_{\langle\langle i,j\rangle\rangle}[r_{ij} - \sqrt{2}(R_i + R_j)]^2, \tag{3}$$

where r_{ij} is the distance between the ith and jth sites, and k_1 is the spring constant (Fig. 1). $\mathcal{H}_{nn}$ expresses elastic interaction between nearest-neighbor pairs ($\langle i, j\rangle$). The interaction is a function of the molecular radius $R_i[= (1 - n_i)R_{\mathrm{LS}} + n_i R_{\mathrm{HS}}]$ of the ith site, where R_{HS} and R_{LS} are the molecular radius of HS and LS states, respectively. We set the ratio of the radii to be $R_{\mathrm{HS}}/R_{\mathrm{LS}} = 1.1$. $\mathcal{H}_{nnn}$ expresses elastic interaction for next-nearest-neighbor pairs ($\langle\langle i, j\rangle\rangle$). In this study, we set the ratio of the spring constants, k_1/k_2, to be 10 [35].

For the simulation, we adopt the NPT-MC method [36] 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, $H = E + PV$, where E is the energy and V is the volume of the system. The states of the system are specified by $4N + 1$ variables $(n_1, \cdots, n_N, \mathbf{r}_1, \cdots, \mathbf{r}_N, V)$. In the NPT-MC method, we have the following detailed balance condition for the transition probabilities $\{w_{i\to k}\}$:

$$\frac{w_{i\to k}}{w_{k\to i}} = \exp(-\beta\Delta W), \tag{4}$$

where

$$\Delta W = (E_k - E_i) + P(V_k - V_i) - NT\log\left(\frac{V_k}{V_i}\right). \tag{5}$$

The scheme of the simulation is as follows. (i) Choose a molecule randomly. (ii) Choose a candidate spin state $n_i = 0$ or 1 with the probability $g_{\mathrm{LS}}/(g_{\mathrm{LS}} + g_{\mathrm{HS}})$ or $g_{\mathrm{HS}}/(g_{\mathrm{LS}} + g_{\mathrm{HS}})$, respectively. (iii) Choose a candidate position of the molecule ($\mathbf{r}_i$). Here, we use the scaled coordination length $\mathbf{s} = \mathbf{r}_i/L$ ($L = V^{1/3}$). We choose the candidate position as, $s_x \to s_x + \delta\xi_x$, $s_y \to s_y + \delta\xi_y$, $s_z \to s_z + \delta\xi_z$, where ξ_x, ξ_y and ξ_z are random numbers between -1 and 1, and $\delta = 0.005$. (iv) Update the state by the Metropolis method. (v) Repeat the above update N times. (vi) Choose a candidate for a new size of the system with a random number ξ_L: $L \to L + \lambda\xi_L$. (vii) Update the size L. Here, λ is taken equal to $0.08N^{1/3}R_{\mathrm{LS}}$. In this study, we performed 10 000 MCSs for transient steps and 10 000 MCSs to measure the physical quantities. The system size is $N = 16 \times 16 \times 16$, which is enough to study thermal properties. Generally, near the critical point the size dependence is important. However, here, we focused on the phase structure but not on the details of the critical properties. We have checked that the data given here show almost no change even when we perform simulations for ($32 \times 32 \times 32$) or 1 000 000 MCSs at several points.

First, we study how the types of temperature dependence of the HS fraction $f_{\mathrm{HS}}(T)$ change with the spring constant $k_1(= 10k_2)$. In Fig. 2 we depict $f_{\mathrm{HS}}(T)$ for various values of k_1 with $g(= g_{\mathrm{HS}}/g_{\mathrm{LS}}) = 20$, $D = 1$, $P = 0.01$, and $k_1 = 10$, 20, 30,40, and 50. When k_1 is small, e.g., $k_1 = 10$, the transition is gradual. As k_1 becomes large, the transition becomes sharp. For $k_1 = 40$, hysteresis appears

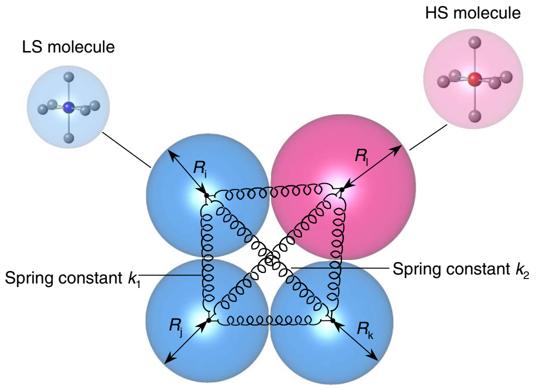

FIG. 1 (color online). Schematic illustration of the present model. HS/LS molecule consists of Fe atom (red/blue circle) and six ligands (gray circles).

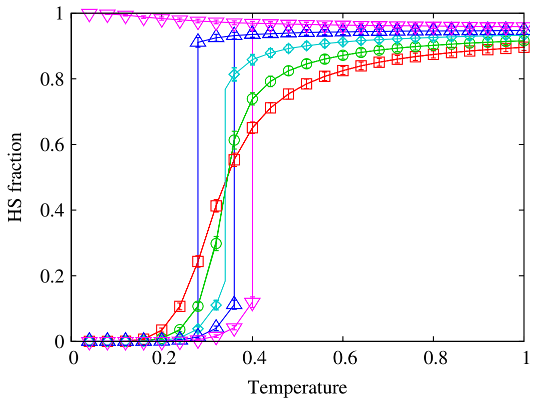

FIG. 2 (color online). Temperature dependence of the HS fraction $f_{\mathrm{HS}}(T)$ with $g = 20$, $D = 1$, $P = 0.01$, and $k_1 = 10$ (red squares), 20 (green circles), 30 (light blue diamonds), 40 (blue triangles), and 50 (pink inverted triangles). Solid lines are guides for the eye.

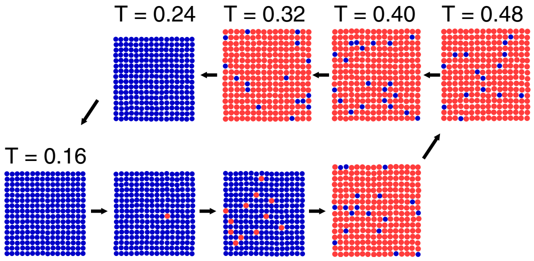

FIG. 3 (color online). Two-dimensional snapshots at various temperatures with $g = 20$, $D = 1$, $P = 0.01$, and $k_1 = 40$. Gray (red online) and black (blue online) circles are HS and LS molecules, respectively.

between cooling and warming processes. Snapshots of the spin configuration (a two-dimensional section of the lattice) are shown in Fig. 3. When k_1 becomes larger, i.e., $k_1 = 50$, the transition does not take place in the cooling process and the HS phase is maintained down to $T = 0$. This observation indicates the existence of a HS metastable phase at low temperatures [20,21]. 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 $f_{\mathrm{HS}}(T)$ that agrees with the generic sequence proposed in our previous papers [20,21,37]. Thus, we expect that both a low-temperature HS metastable phase and a thermal hysteresis are observed. 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 $T = 0.36$. Therefore, we find that the HS metastable phase and hysteresis are both observed.

Next, we study the pressure effect on $f_{\mathrm{HS}}(T)$. In Fig. 5, we depict $f_{\mathrm{HS}}(T)$ during the warming process from the HS state. In the case of low pressure, $P = 0.01$, the state is always in the HS state and the transition is not observed. When the pressure becomes $P = 0.1$, the initial HS state is metastable and the state shows hysteresis at high temperatures. 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. When the pressure increases further, $P = 0.5$, the transition becomes gradual. We define $T_{1/2}$ at which $f_{\mathrm{HS}} = 1/2$. In the hysteresis region, we define it as the temperature where $(1/2 - f_{\mathrm{HS}})$ in the warming process is equal to the $(f_{\mathrm{HS}} - 1/2)$ 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.

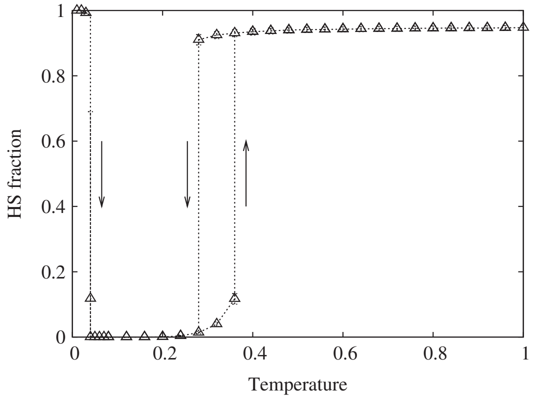

FIG. 4. Temperature dependence of the HS fraction with $g = 20$, $D = 1$, $P = 0.01$, and $k_1 = 40$. Dotted line is a guide for the eye.

We also study the pressure dependences of $f_{\mathrm{HS}}(T)$ at various temperatures. In Fig. 6, $f_{\mathrm{HS}}(T)$ 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. In the case $T = 0.3$, a transition from the HS to the LS phases takes places at $P = 0.1$ [red (i) arrow]. In the process of reducing pressure [red (ii) arrow], this pressure-induced LS phase does not return to the HS phase. Although this LS state is the equilibrium state at low temperature, it is difficult to access to it by simply reducing the temperature. The present realization of the LS state by pressure indicates a new control of the spin state. At $T = 0.5$, a pressure-induced hysteresis is observed. The transition is smooth at $T = 0.7$. The present observations indicate that the pressure plays a similar role to that of the temperature for the SC transition.

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 $f_{\mathrm{HS}}(T)$ as a function of the pressure which agrees with that proposed as the generic sequence of SC transitions.

In the present study, we kept the parameters D and g constant. If we take into account pressure dependence of

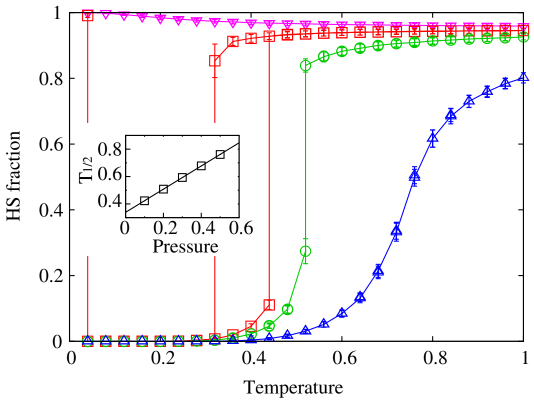

FIG. 5 (color online). Temperature dependence of HS fraction with $g = 20$, $D = 1$, $k_1 = 50$, and $P = 0.01$ (pink inverted triangles), 0.1 (red squares), 0.2 (green circles), 0.5 (blue triangles). Inset is the pressure dependence of $T_{1/2}$. Solid lines are guides for the eye.

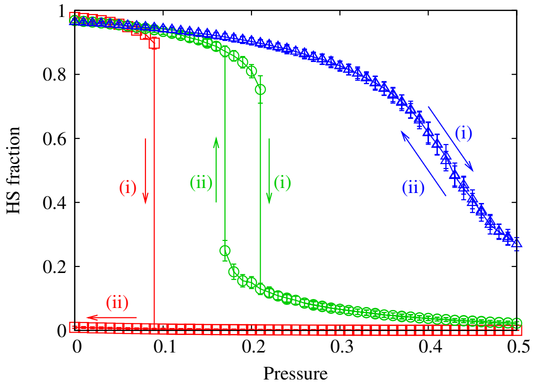

FIG. 6 (color online). Pressure dependence of the HS fraction with $g = 20$, $D = 1$, $k_1 = 50$, and $T = 0.3$ (red squares), 0.5 (green circles), and 0.7 (blue triangles). The numbered arrows indicate the pressure sequence. Solid lines are guides for the eye.

these parameters, 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 with the present model and attempt to obtain a systematic understanding of the variety of pressure effects on the SC transitions.

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