

## Structures of Metastable States in Phase Transitions with a High-Spin Low-Spin Degree of Freedom

Seiji MIYASHITA,<sup>1,\*</sup> Yusuke KONISHI,<sup>1,\*\*</sup> Hiroko TOKORO,<sup>1,\*\*\*</sup> Masamichi NISHINO,<sup>2,†</sup> Kamel BOUKHEDDADEN<sup>3,††</sup> and François VARRET<sup>3,†††</sup>

<sup>1</sup>*Department of Physics, School of Science, The University of Tokyo,  
Tokyo 113-8656, Japan*

<sup>2</sup>*Computational Materials Science center, National Institute for Materials Science,  
Tsukuba 305-0047, Japan*

<sup>3</sup>*Laboratoire de Magnétisme et d'Optique, Université de Versailles  
Saint-Quentin-en-Yvelines, 45 Avenue des Etats Unis 78035 Versailles, France*

(Received April 23, 2005)

The difference in the degeneracy of low-spin (LS) and high-spin (HS) states causes interesting entropy effects on spin-crossover phase transitions and charge transfer phase transitions in materials composed of spin-crossover atoms. Mechanisms of the spin-crossover (SC) phase transitions have been studied using the Wajnflasz model, where the degeneracy of the spin states (HS or LS) is taken into account, and the cooperative nature of the spin-crossover phase transitions has been well described. Recently, a charge transfer (CT) phase transition due to electron hopping between LS and HS sites has been studied using a generalized Wajnflasz model. Systems with SC and CT both have a high temperature structure (HT) and a low temperature structure (LT), and the transition between them can be a smooth crossover or a discontinuous first-order phase transition, depending on the parameter values of the systems. Although, apparently, the standard SC system and the CT system are very different, it has been shown that the two models are equivalent under a certain transformation of variables. In both systems, the structure of the metastable state at low temperatures is a matter of interest. We study the temperature dependence of the fraction of HT systematically in a unified model and find several structures of equilibrium and metastable states of the model as functions of the system parameters. In particular, we find a reentrant-type metastable branch of HT in a low temperature region, which could play an important role in the study of the photo-irradiated processes of related materials.

### §1. Introduction

In so-called spin-crossover atoms, e.g., Fe and Co, spin states of the atoms can change between the high-spin (HS) state and the low-spin (LS) state as a result of small perturbations, such as changes of temperature or pressure, photo-irradiation, etc. This change of the spin state is called a spin-crossover (SC) transition.<sup>1)–38)</sup> The HS state has a large degeneracy, and it is favorable at high temperatures, while the LS state has a low energy, which is favorable at low temperatures. The competition

---

<sup>\*</sup>) E-mail: miyashita@phys.s.u-tokyo.ac.jp

<sup>\*\*</sup>) E-mail: konishi@spin.phys.s.u-tokyo.ac.jp

<sup>\*\*\*</sup>) E-mail: tokoro@spin.phys.s.u-tokyo.ac.jp

<sup>†</sup>) E-mail: NISHINO.Masamichi@nims.go.jp

<sup>††</sup>) E-mail: kbo@physique.uvsq.fr

<sup>†††</sup>) E-mail: fvarret@physique.uvsq.fr

between the effects of degeneracy (the entropy) and of the energy provides interesting variations in the structure of ordering processes.

From the point of view of adiabatic energy levels of the local structure of atoms, the population dynamics among states (HS, LS, and other excited states) under photo-irradiation has been studied with a kind of rate equation, which accounts for the mechanism of the transitions among the LS and HS states.<sup>13),14)</sup> It has also been pointed out that cooperative interactions are important for SC transitions. With the influence of interactions between atoms, this transition can be either a smooth crossover or a discontinuous first-order phase transition, depending on the system parameters.<sup>1)-3),19)-32),38)</sup> This situation is described by the Wajnflasz model.<sup>38)</sup> Control of the transition between the HS and LS states has been realized by use of photo-irradiation through light-induced excited spin state trapping (LIESST).<sup>12)-18),33)-37)</sup> Given this situation, the structure of the metastable ordered state of the systems has become an important topic.<sup>18),39)-42)</sup>

Prussian blue analogues (PBAs), classified as molecule-based magnets,<sup>43)-50)</sup> exhibit various photomagnetic phenomena.<sup>51)-59)</sup> Two-way photo-switching between magnetic and nonmagnetic states has been observed in a Co-Fe Prussian blue analogue,  $\text{K}_{0.2}\text{Co}_{1.4}\text{Fe}(\text{CN})_6 \cdot 6.9\text{H}_2\text{O}$ ,<sup>52),53)</sup> which has attracted much interest. This photomagnetism is based on the charge-transfer-induced spin transition (CTIST) between two phases,<sup>55)</sup> e.g., the high temperature (HT) phase consisting mainly of  $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ , where  $\text{Co}^{\text{II}}$  is in the high spin state (HS,  $S = 3/2$ ) and  $\text{Fe}^{\text{III}}$  is in the low spin state (LS,  $S = 1/2$ ), and the low temperature (LT) phase consisting mainly of  $\text{Co}^{\text{III}}\text{-Fe}^{\text{II}}$ , where  $\text{Co}^{\text{III}}$  is in the low spin state (LS,  $S = 0$ ) and  $\text{Fe}^{\text{II}}$  is also in the low spin state (LS,  $S = 0$ ). In this material, Co and Fe ions are antiferromagnetically coupled. Therefore, precisely speaking, it is a ferrimagnetic material. However, a spin-crossover transition occurs at the Co site, and if we consider a unit consisting of a pair atoms (Fe and Co), we can regard the transition as a generalized SC transition.

Another type of phase transition due to charge transfer (CT) was discovered in a mixed-valence iron complex  $(\text{n-C}_3\text{H}_7)_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$  ( $\text{dto} = \text{C}_2\text{O}_2\text{S}_2$ ).<sup>60)-62)</sup> In this material, charge transfer causes a change of the degeneracy of the atomic states, and a phase transition occurs between the high temperature (HT) and low temperature (LT) structures. In this system, there is no spin transition for each atom. However, the entropy effect has an important role in determining the structure change of the electron configuration, and the nature of the phase transition was explained using a generalized Wajnflasz model.<sup>62)</sup> There, it was found that a metastable branch of HT structure exists at all temperatures below the critical temperature. This behavior is qualitatively different from that found in the standard model of the SC transition. That is, due to the fact that experimentally it is known that the fraction of HS exhibits a hysteresis loop in SC transitions, for SC transitions we have adopted a model in which the metastable branch of HS terminates at a spinodal point, below which the HS is unstable. In this model, it is difficult to explain the metastable behavior of the photo-induced HS state at low temperatures. In order to overcome this difficulty, a dynamical effect has been introduced by adopting the so-called Arrhenius dynamics.<sup>33)</sup> This effect is able to account for the fact that the HS state remains for a long time at low temperatures, although it is unstable if we

consider only the mean-field free energy.<sup>35)–37)</sup> Contrastingly, in the model of CT, the HT state is metastable at all the temperatures. In view of these results, it is an interesting problem to study the relation between the two models.

In this paper, we show that the two models are equivalent under a certain transformation of a variable, and that the unified model exhibits several qualitatively different structures of equilibrium and metastable states as a function of the system parameters. In particular, a reentrant-type metastable branch of HT structure in a low temperature region is discovered. The existence of this low temperature metastable structure should play an important role in the study of photo-irradiated processes of related materials. Here, we mainly study the transition between spin states, e.g., HS  $\Leftrightarrow$  LS. However, if we consider magnetic interactions between spins, the structure of the phase transition is modified. The magnetic effect has been studied for Co-Fe PBA.<sup>36), 37), 40), 41)</sup> The magnetic phase transition in the CT system has also been studied.<sup>62)–64)</sup> It has been found that the existence of metastable states creates new type of magnetic phase transition, which is discussed briefly.

## §2. Unified model

### 2.1. Typical spin-crossover phase transition with a single hysteresis

In order to describe the spin-crossover transition, the so-called Wajnflasz model has been adopted.<sup>38)</sup> In this model, the HS state is represented by  $s = 1$ , and the LS state is represented by  $s = -1$ . It should be noted that the states  $s_i = \pm 1$  have different degeneracy. Let the number of states of the HS state be  $n_H$ , and that of the LS state be  $n_L$ . Let us review the Wajnflasz model briefly. The interactions among atoms originate in the elastic interaction in the atomic structure.<sup>23)</sup> However, here it is simply modeled by a nearest-neighbor interaction between sites, and the Hamiltonian has the form

$$\mathcal{H}_W = -J \sum_{\langle ij \rangle} s_i s_j + D \sum_i s_i, \quad (2.1)$$

where  $J$  denotes the interaction between states of neighboring atoms, and  $D$  denotes the energy difference between HS and LS. Here we consider the case  $D > 0$ ; i.e., the LS state is energetically favorable. The partition function is given by

$$Z = \text{Tr} e^{-\beta \mathcal{H}_W} = \sum_{s_1 = \pm 1} \cdots \sum_{s_N = \pm 1} \exp \left( \beta J \sum_{\langle ij \rangle} s_i s_j - \beta D \sum_i s_i \right), \quad (2.2)$$

where the summation  $\sum'$  is carried out over the degenerate states, i.e., over the  $n_H$  states with  $s_i = 1$  and the  $n_L$  states with  $s_i = -1$ . Here,  $\beta = 1/k_B T$ , and  $N$  is the number of sites. This form is expressed in terms of a non-degenerate Ising variable  $\sigma_i = \pm 1$  as

$$Z = \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} \exp \left( \beta J \sum_{\langle ij \rangle} \sigma_i \sigma_j - \beta D \sum_i \sigma_i \right) \prod_i (n_H \delta_{\sigma, 1} + n_L \delta_{\sigma, -1}). \quad (2.3)$$

We may rewrite the second factor as

$$n_H \delta_{\sigma,1} + n_L \delta_{\sigma,-1} = \sqrt{n_H n_L} e^{\frac{1}{2} \sigma \ln \frac{n_H}{n_L}}. \quad (2.4)$$

Now we have

$$Z = (n_H n_L)^{\frac{N}{2}} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \exp \left( \beta \left( J \sum_{\langle ij \rangle} \sigma_i \sigma_j - \left( D - \frac{k_B T}{2} \ln g \right) \sum_i \sigma_i \right) \right), \quad (2.5)$$

and

$$g = \frac{n_H}{n_L}. \quad (2.6)$$

Therefore, the Hamiltonian (2.1) can be expressed as the following effective Hamiltonian with a temperature dependent field

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j + \left( D - \frac{k_B T}{2} \ln g \right) \sum_i \sigma_i. \quad (2.7)$$

The model employing this form of the Hamiltonian is called the Wajnflasz model.

Here, we note a characteristic property of this model. At high temperatures, i.e., for  $k_B T > 2D/\ln g$ , the term representing the effective field ( $H_{\text{eff}} = -D + k_B T \ln g/2$ ) is positive, and thus the spins have a positive expectation value,  $\langle \sigma_i \rangle > 0$ .

Contrastingly, at low temperatures, i.e., for  $k_B T < 2D/\ln g$ , we have  $\langle \sigma_i \rangle < 0$ . Let us define the marginal temperature  $T_0$  by

$$k_B T_0 = \frac{2D}{\ln g}, \quad (2.8)$$

where  $\langle \sigma_i \rangle = 0$ . If  $T_0$  is larger than the critical temperature  $T_{\text{IC}}$  of the corresponding Ising model, whose Hamiltonian is

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j, \quad (2.9)$$

that is,

$$T_0 > T_{\text{IC}}, \quad (2.10)$$

then the change of the magnetization is smooth. By contrast, if

$$T_0 < T_{\text{IC}}, \quad (2.11)$$

then a discontinuous change occurs, which means first-order phase transition takes place.

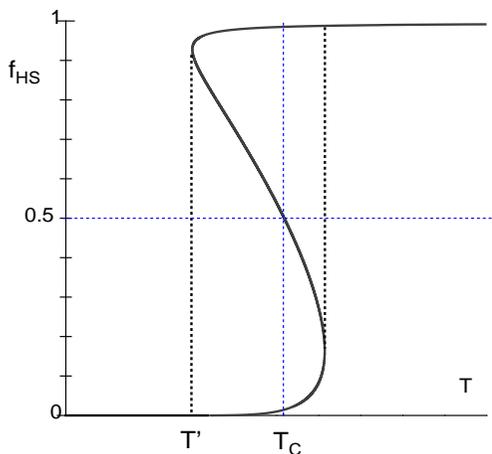


Fig. 1. Schematic temperature dependence of a solution to the self-consistent of equation of a mean-field theory for a high spin fraction  $q$  in models of the SC transition with a hysteresis loop. The bold dotted curve represents the hysteresis region. The thin dotted line indicates the first-order phase transition temperature where  $q = 0.5$ .

A typical example of the hysteresis obtained through a kind of mean field analysis is schematically depicted in Fig. 1. To this time, experimental results regarding the first-order phase transition have been described using this type of temperature dependence of the order parameter  $f_{\text{HS}} (= (\langle \sigma_i \rangle + 1)/2)$ , which is the fraction of the atoms in the HS state. In this figure, the HS state becomes unstable at a temperature  $T'$ , denoted by the dotted line. Below this temperature, the HS state is unstable. Thus, it seems unfeasible to have a long-lived HS state at low temperatures. In Co-Fe PBA, however, the magnetic state exists for a long time after pumping by photo-irradiation. In order to explain this long-lived state, we have introduced a mechanism causing very slow dynamics, the so-called Arrhenius dynamics,<sup>33),37)</sup> in which we assume an Arrhenius-type relaxation time,  $\tau \propto \exp(-E_0/k_{\text{B}}T)$ , with an appropriate value of  $E_0$ .

## 2.2. Metastable structure of a charge transfer phase transition

In contrast to the behavior discussed above, we have found a case in which static metastability exists in a study of the charge transfer transition in the material  $(\text{nC}_3\text{H}_7)_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$  ( $\text{dto}=\text{C}_2\text{O}_2\text{S}_2$ ).<sup>60)-62)</sup> Here, let us consider this charge transfer transition. This material consists of a bipartite lattice. In one of the sublattices, Fe is surrounded by sulphur atoms, and here, Fe is always in the LS state, while in the other sublattice, Fe is surrounded by oxygen atoms, and here Fe is always in the HS state. We call a site in the former sublattice an ‘A-site’ and a site in the latter sublattice a ‘B-site’. Let both sublattices have  $N$  sites. Because  $\text{Fe}^{\text{II}}$  has one more electron than  $\text{Fe}^{\text{III}}$ , the difference between them can be expressed by the number of additional electrons  $n_i$ , which is 1 for  $\text{Fe}^{\text{II}}$  and 0 for  $\text{Fe}^{\text{III}}$ . Here, we consider the degeneracy of the spin degree of freedom.<sup>62)</sup> At an A-site,  $\text{Fe}^{\text{II}}$  is in the low spin state and  $S = 0$ , as depicted in Fig. 2, and thus the degeneracy is 1, and the spin of  $\text{Fe}^{\text{III}}$  is  $S = 1/2$ , and thus its degeneracy is 2. Similarly at a B-site,  $S = 2$  for  $\text{Fe}^{\text{II}}$  and  $S = 5/2$  for  $\text{Fe}^{\text{III}}$ . In terms of  $\{n_i\}$ , the degeneracy is given as follows:

site	$n$	spin $S$	degeneracy
A	$n = 1$	0	$n_{\text{A}1}=1$
A	$n = 0$	1/2	$n_{\text{A}0}=2$
B	$n = 1$	2	$n_{\text{B}1}=5$
B	$n = 0$	5/2	$n_{\text{B}0}=6$

Because the numbers of sites of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  are the same, the total number of additional electrons is  $N$

$$\sum_i n_i = N. \quad (2.12)$$

In this material, electrons are transferred between A and B sites. We have introduced the following Hamiltonian for this system:

$$\mathcal{H}_{\text{CT}} = \varepsilon \sum_{\langle ij \rangle} n_i n_j + \Delta \sum_{i \in \text{B}} n_i. \quad (2.13)$$

Here,  $\varepsilon$  represents the interaction between the electrons at nearest-neighbor sites. The quantity  $\Delta (> 0)$  is a kind of local on-site energy. Because of this term, ener-

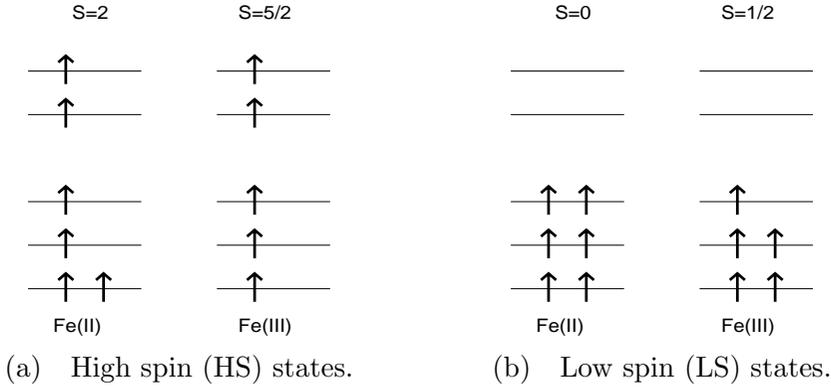


Fig. 2. Electron states of Fe<sup>II</sup> and Fe<sup>III</sup> in (a) the high spin (HS) state and (b) the low spin (LS) state.

getically electrons tend to stay at A-sites. If all the electrons are at A-sites, then there is no energy cost due to  $\Delta$ . Therefore, we define this state as a perfect LT state. Because of the difference in degeneracy mentioned above, at high temperature, electrons tend to stay at B-sites. We represent the degree for which the system is in the high temperature (HT) state by the number of electrons at B-sites,

$$\langle n_B \rangle = \frac{\sum_{i \in B} n_i}{N}. \quad (2.14)$$

In the above choice of the degeneracy,  $\langle n_B \rangle$  is more than 1/2 at high temperatures. In the present model, no spin-crossover transition occurs through electron transfer. However, the degeneracy of spins still plays an important role, and this model exhibits a first-order phase transition.<sup>62)</sup> In the mean field theory, the self-consistent equation for  $q = \langle \sigma_{i \in B} \rangle$  is given by

$$q = \tanh \left[ \beta \left( \frac{z\varepsilon q}{4} - \frac{\Delta}{4} + k_B T \ln(5/3) \right) \right], \quad (2.15)$$

where  $z$  is the number of nearest-neighbor sites, which is 3 for a honeycomb lattice. We depict a typical temperature dependence of a solution of the self-consistent equation for  $\langle n_B \rangle = (q + 1)/2$  in Fig. 3 for  $\Delta = 1$  and 10. There, we fix  $\varepsilon$  to 3. As shown in Fig. 3(b), there are three solutions for  $q$  at low temperatures. There, the solution with the largest and smallest values of  $\langle n_B \rangle$  are stable, and that with the intermediate value of  $\langle n_B \rangle$  is unstable. By comparing the free energies corresponding to them, we find the first-order phase transition point, which is  $T_0$ . In the figures, the temperature at which  $\langle n_B \rangle = 0.5$  is indicated by the dotted lines. This temperature has the same physical meaning as  $T_0$  defined in (2.8), as will be shown in the following subsections.

Here we again find that there are cases in which the change is smooth and cases in which it is discontinuous. However, in this charge transfer transition, the metastable branch of the HT state remains until  $T = 0$ ; i.e., the HT state is metastable even at very low temperatures.

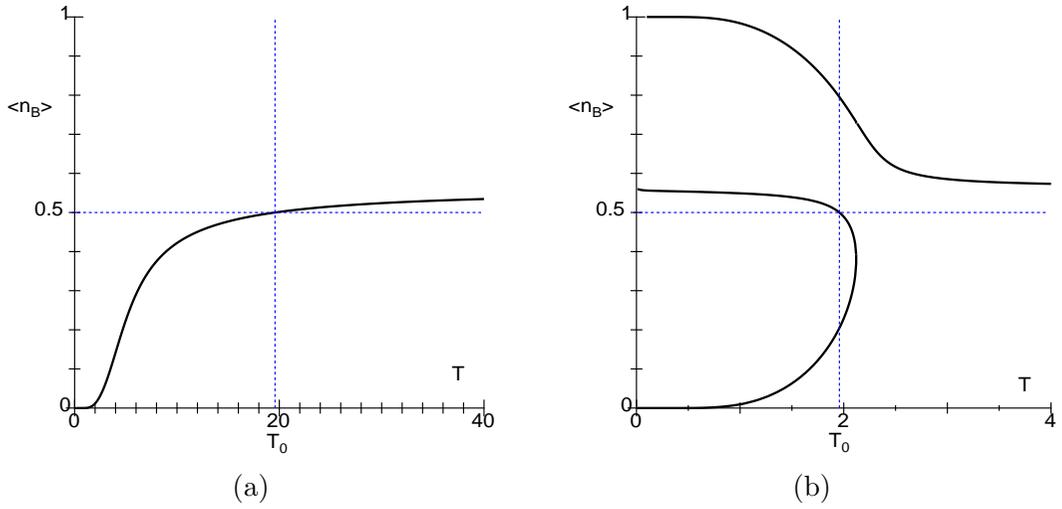


Fig. 3. Temperature dependence of the fraction of the HT state  $\langle n_B \rangle$  for systems with  $\varepsilon = 3$ . (a)  $\Delta = 10$  and (b)  $\Delta = 1$ . Here,  $T_0$  is the temperature in the case  $\langle n_B \rangle = 0.5$ , and it is also the critical temperature in the case (b).

### 2.3. Comparison

In the two observations made with regard to the above SC and CT cases, there are qualitatively different temperature dependences of the free energy structure. Thus, it would be interesting to compare these two cases. Here, we attempt to express the model with the Hamiltonian given in (2.13) in the form of the Wajnflasz model, whose Hamiltonian is given in (2.7).

First, we transform the variable  $n_i$  ( $= 0$  or  $1$ ) to  $s_i$  ( $= -1$  or  $1$ ), using the relation

$$n_i = \frac{s_i + 1}{2}. \tag{2.16}$$

Then, the constraint  $\sum_i n_i = N$  becomes

$$\sum_i s_i = 0. \tag{2.17}$$

Also the Hamiltonian becomes

$$\mathcal{H} = \frac{\varepsilon}{4} \sum_{\langle ij \rangle} (s_i + 1)(s_j + 1) + \frac{\Delta}{2} \sum_{i \in B} (s_i + 1). \tag{2.18}$$

Making use of the constraint (2.17) we can rewrite this as

$$\mathcal{H} = \frac{\varepsilon}{4} \sum_{\langle ij \rangle} (s_i + 1)(s_j + 1) + \frac{\Delta}{4} \left( \sum_{i \in B} (s_i + 1) - \sum_{i \in A} (s_i + 1) \right). \tag{2.19}$$

In order to obtain a ferromagnetic model, we perform a local gauge transformation by taking  $\varepsilon \rightarrow -\varepsilon$  and  $s_i \rightarrow -S_i$  at each A-site and  $s_i \rightarrow S_i$  at each B-site. Then we

have

$$\mathcal{H} = -\frac{\varepsilon}{4} \sum_{\langle ij \rangle} S_i S_j + \frac{\Delta}{4} \left( \sum_{i \in A} S_i + \sum_{i \in B} S_i \right). \quad (2.20)$$

Here we again use the non-degenerate Ising variable  $\sigma_i$ . It should be noted that the degree of degeneracy at A- and B-sites are different. However, using relations similar to (2.4), the these degrees ( $n_{A1}$ ,  $n_{A0}$ ,  $n_{B1}$  and  $n_{B0}$ ) can be taken into account as

$$\mathcal{H} = -\frac{\varepsilon}{4} \sum_{\langle ij \rangle} \sigma_i \sigma_j + \left( \frac{\Delta}{4} + \frac{1}{2} k_B T \ln \frac{n_{A1}}{n_{A0}} \right) \sum_{i \in A} \sigma_i + \left( \frac{\Delta}{4} - \frac{1}{2} k_B T \ln \frac{n_{B1}}{n_{B0}} \right) \sum_{i \in B} \sigma_i. \quad (2.21)$$

Then, using the constraint

$$\sum_{i \in A} \sigma_i - \sum_{i \in B} \sigma_i = 0, \quad (2.22)$$

we finally have

$$\mathcal{H} = -\frac{\varepsilon}{4} \sum_{\langle ij \rangle} \sigma_i \sigma_j + \left( \frac{\Delta}{4} + \frac{1}{4} k_B T \ln \frac{g_A}{g_B} \right) \sum_i \sigma_i, \quad (2.23)$$

where  $g_A = n_{A1}/n_{A0}$  and  $g_B = n_{B1}/n_{B0}$ . Now, the Hamiltonian is in the same form as that of the Wajnflasz model (2.7). Therefore, it is proved that the model with the Hamiltonian (2.13) is equivalent to the model with the Hamiltonian (2.1).

#### 2.4. $T_0$ for the CT transition

In this formalism, we can make use of the relation (2.8) to distinguish the smooth and discontinuous changes. Here, the transition temperature  $T_0$  is given by

$$k_B T_0 = \frac{\Delta}{\ln \frac{g_B}{g_A}}. \quad (2.24)$$

Substituting the degrees of degeneracy, we have

$$k_B T_0 = \frac{\Delta}{\ln \frac{5/6}{1/2}} = \frac{\Delta}{\ln 5/3} \simeq 1.958 \Delta. \quad (2.25)$$

In this subsection, we set  $k_B = 1$ .

In the case  $\Delta = 10$ , the condition (2.10) is satisfied. That is, in a honeycomb lattice, the critical temperature of the ferromagnetic Ising model is given by  $k_B T_{CI} = 3(\varepsilon/4)$  in the mean-field theory, and therefore, for  $\varepsilon = 3$ , we have

$$T_{CI} = 0.75 \times 3 < T_0 = 1.958 \times 10, \quad (2.26)$$

and thus  $\langle n_B \rangle$  changes smoothly, as depicted in Fig. 3(a). Contrastingly, for  $\Delta = 1$ , we have

$$T_{CI} = 0.75 \times 3 > T_0 = 1.958 \times 1, \quad (2.27)$$

and the transition is first order, as depicted in Fig. 3(b).

## 2.5. Monte Carlo study

It should be noted that, although in the above, we studied the model in the mean-field approximation, the criterion for whether the change of  $\langle n_B \rangle$  at  $T_0$  is smooth or discontinuous, i.e., the relation between  $T_0$  and  $T_{CI}$ , also holds in the exact treatment. In the above treatment, the value of  $T_0$  is given in the mean-field approximation because we studied the model in the mean-field approximation. However, in the exact treatment,  $T_0$  is given by the critical temperature of the ferromagnetic Ising model,

$$T_{CI} = \frac{2}{\ln(2 + \sqrt{3})} \frac{\varepsilon}{4} \simeq 1.52 \times \left( \frac{\varepsilon}{4} \right). \quad (2.28)$$

In Fig. 4, we depict the temperature dependence of  $\langle n_B \rangle$  studied using a Monte Carlo (MC) method for  $\varepsilon = 3$  and 6 with  $\Delta = 1$ . Because we study the exact short range model in this MC method, we find exact properties, although the result is numerical. For  $\varepsilon = 3$ , we find

$$T_{CI} = 1.52 \times (3/4) < T_0 = 1.958, \quad (2.29)$$

and therefore we indeed find that  $\langle n_B \rangle$  changes smoothly, as plotted by the open circles. For a discontinuous change of  $\langle n_B \rangle$ , the relation  $T_0 < T_{CI}$ , i.e.,

$$1.958 < 1.52 \times (\varepsilon/4), \quad (2.30)$$

must hold. Therefore, in the MC treatment,  $\varepsilon$  must be larger than 5.15 ( $= 1.958 \times 4/1.52$ ) for a discontinuous change. The temperature dependence of  $\langle n_B \rangle$  for  $\varepsilon = 6$  is also plotted in Fig. 4 by dots. There we find a discontinuous jump. Here, we changed the value of  $\varepsilon$  instead of  $\Delta$  to obtain the same value of  $T_0$  for convenience in plotting.

Monte Carlo simulations were performed with a honeycomb lattice of size  $32 \times 32$ . The simulation started at  $T = 0.125$ , where  $\langle n_B \rangle \simeq 0$  in the equilibrium state. The temperature was increased up to  $T = 4$ . At each temperature, we first carried out 20,000 Monte Carlo steps (MCS), which were regarded as a transient process, and then we took data in the subsequence 100,000 MCS. The fluctuations of the data are smaller than the size of the dots.

We find that  $\langle n_B \rangle$  jumps at  $T = 2.12$ , although the exact critical point is  $T_0 = 1.958$ , which is indicated by the dotted line, where  $\langle n_B \rangle = 0.5$ . This shift of the jump is due to the hysteresis phenomenon associated with the first-order phase transition.

After  $T = 4$ , the temperature was reduced. We find almost the same values of  $\langle n_B \rangle$  as those in the heating process above  $T = 2.12$ . However,  $\langle n_B \rangle$  retains a

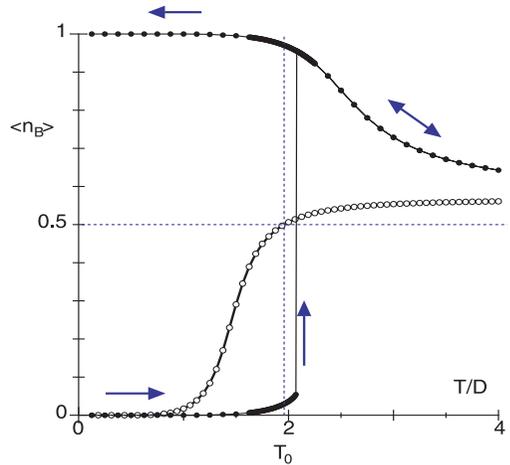


Fig. 4. Temperature dependence of the fraction of the system in the HT state  $\langle n_B \rangle$  for  $\varepsilon = 3$  (open circles) and 6 (dots) obtained through Monte Carlo simulations. Here,  $\Delta = 1$ .

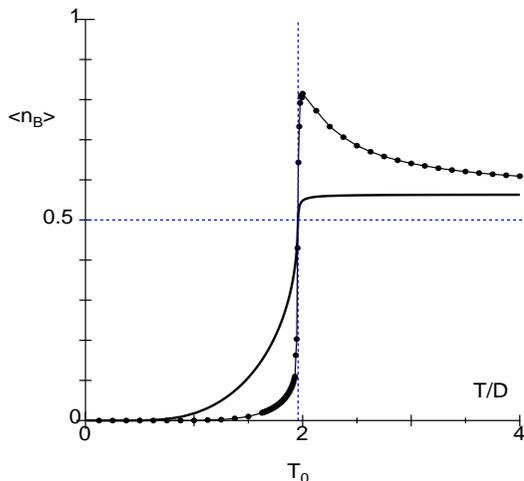


Fig. 5. Temperature dependence of the fraction of the system in the HT state  $\langle n_B \rangle$  at the critical value of  $\varepsilon$ , as obtained using the mean-field theory, with  $\varepsilon_C = 3/(4 \ln 10/3) = 2.61 \dots$ , and Monte Carlo simulations, with  $\varepsilon_C = 1/(4 \ln 10/3) = 5.18 \dots$ . Here,  $\Delta = 1$ .

in the exact treatment and also in the Monte Carlo simulation. In the mean-field theory, on the other hand, the critical exponents are  $\delta = 3$  and  $\beta = 1/2$ . In Fig. 5, the temperature dependences of  $\langle n_B \rangle$  at the critical value of  $\varepsilon$  are plotted for both cases studied using the mean-field theory (by the bold curve) and using the MC simulation (by the circles). Here it should be noted that  $\langle n_B \rangle$  displays a non-monotonic temperature dependence even in the case of a second-order phase transition obtained with the MC method.

### §3. Classification of the temperature dependence of the high-spin fraction

In the previous section, we have found the equivalence of the model of the SC transition and the model of the CT transition. In the SC case, the HS state becomes unstable at a temperature  $T'$  below the hysteresis loop. Contrastingly, in the CT case, the HT state remains metastable below  $T_0$ , until  $T = 0$ . These two observations suggest that there are qualitatively different temperature dependences of the free energy structure. By studying these structures, we can reach a comprehensive understanding of phase transitions in systems of spin-crossover atoms.

Here we study a model of the type of (2.7), with the variable  $\sigma_i = \pm 1$ :

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j + \left( D - \frac{k_B T}{2} \ln g \right) \sum_i \sigma_i. \quad (3.1)$$

As mentioned in the previous section, the temperature  $T_0$  at which  $\langle \sigma_i \rangle = 0$  is given by (2.8). Here, we define  $D_C$  by the condition that the system exhibits a first-order

large value below this temperature, and it remains in the metastable HT state even below  $T_0$ . This metastability corresponds to the metastable solution found in the mean field theory. In the case  $\varepsilon = 3$ , no hysteresis is found.

In this way, we can determine various properties of  $\langle n_B \rangle$  from knowledge of the corresponding Ising model. For example, at the critical value of  $\varepsilon$ ,  $\langle n_B \rangle$  exhibits a second-order phase transition, where

$$\langle n_B \rangle - \frac{1}{2} \propto |T - T_0|^{\frac{1}{\delta}}, \quad \delta = 15, \quad (2.31)$$

and above the critical value of  $\varepsilon$ ,  $\langle n_B \rangle$  changes discontinuously. The jump of  $\langle n_B \rangle$  is given by

$$\langle n_B(T_0 + 0) - n_B(T_0 - 0) \rangle \propto |\varepsilon - \varepsilon_c|^\beta, \quad \beta = \frac{1}{8}, \quad (2.32)$$

phase transition when  $D < D_C$ :

$$D_C = \frac{k_B T_C}{2} \ln g. \quad (3.2)$$

Next, we consider the condition for the metastability of the HT state in the ground state. By flipping one spin in the configuration in which all the spins are +1, the system gains a crystal field  $-2D$ , while it loses an exchange energy  $2zJ$ , where  $z$  is the number of nearest neighbors. Thus, if  $D$  is smaller than the critical value,

$$D_{CG} = zJ, \quad (3.3)$$

the state in which all spins are +1 is metastable at  $T = 0$ .

Let us study the temperature dependence of the solution(s)

$$q(T) = \langle \sigma_i \rangle \quad (3.4)$$

of the mean-field self-consistent equation,

$$q = \tanh \left[ \beta \left( Jzq - D + \frac{k_B T}{2} \ln g \right) \right]. \quad (3.5)$$

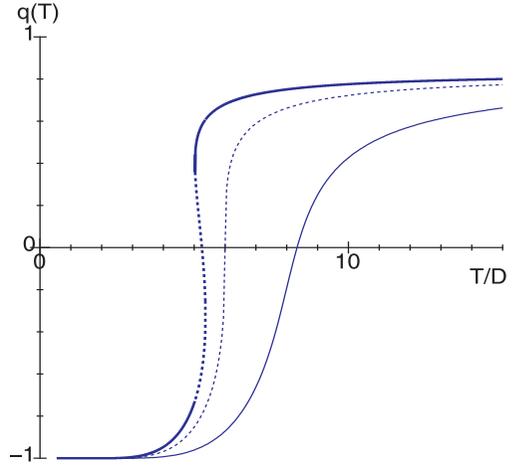


Fig. 6. Temperature dependences of  $q(T)$  for  $D = 10.0$  (thin solid curve),  $D = 7.2$  (dashed curve), and  $D = 6.3$  (bold solid and dashed curve). Here,  $J = 1$  and  $\alpha = 1.2$  ( $g = e^{2.4}$ ).

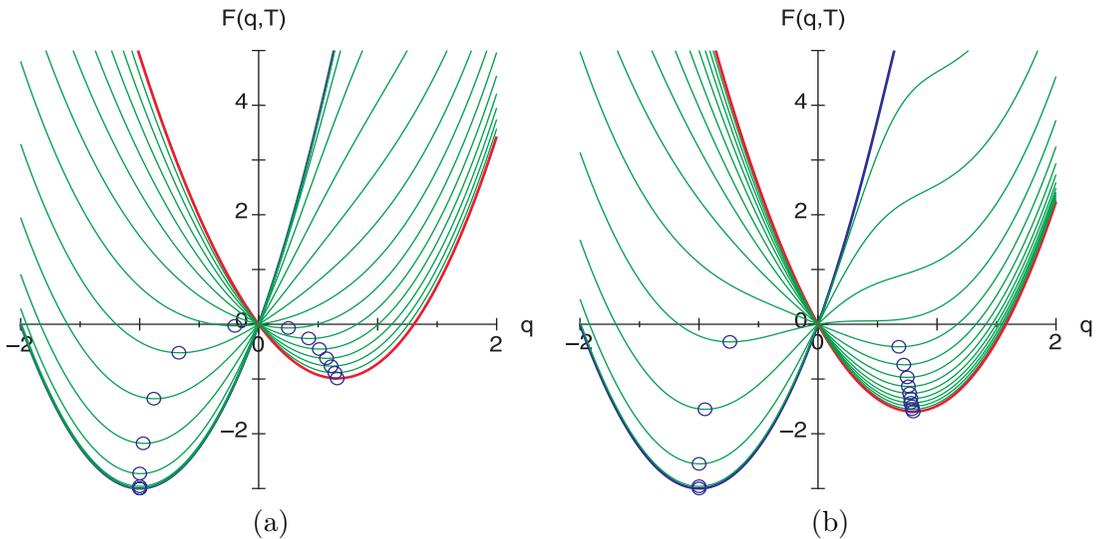


Fig. 7. Temperature dependence of the free energy of functions of  $q$  for (a)  $D = 10.0$ , and (b)  $D = 6.3$ . The temperature changes in jumps of 1 from  $T = 15$  (red) to 1 (blue). Here  $J = 1$  and  $\alpha = 1.2$  ( $g = e^{2.4}$ ). The open circles indicate extreme points of the free energy.

The free energy for this solution is given by

$$F(q) = \frac{1}{2}zJq^2 - k_{\text{B}}T \ln \left[ 2 \cosh \left( \frac{Jzq - D}{k_{\text{B}}T} + \alpha \right) \right]. \quad (3.6)$$

Here, we adopt the parameter values

$$J = 1, \quad z = 6 \quad \text{and} \quad \alpha \equiv \frac{1}{2} \ln g = 1.2, \quad (3.7)$$

and we take  $J$  as the unit of energy. In the following, we study the temperature dependence of  $q(T)$  and its dependence on  $D$ .

### 3.1. Large $D$ behavior

In Fig. 6, we plot the temperature dependence of  $q$  for  $D = 10$  by a thin solid curve. We find a smooth change of  $q$ , and the corresponding temperature dependence of the free energy  $F(q) - F(0)$  is depicted in Fig. 7(a). In the present case,  $D_{\text{C}}$  is 7.2. Below this value, the system exhibits a first-order phase transition. The temperature dependence of  $q(T)$  for  $D = 7.2$  is depicted by the dotted curve. The temperature dependence of  $q$  for  $D = 6.3$  is depicted by the bold solid and dashed curves. This reveals a first-order phase transition. The overhanging part is plotted by a bold dotted curve. This temperature dependence corresponds to the standard phenomena of the HS-LS transition displayed in Fig. 1. The corresponding temperature dependence of the free energy is depicted in Fig. 7(b).

In typical spin-crossover transitions, the ratio of the degeneracy  $g$  is considered to be rather large, and it causes the value of  $q$  in the high temperature limit,

$$q(\infty) = \tanh(\alpha) = \frac{g - 1}{g + 1}, \quad (3.8)$$

to be large.

### 3.2. Hysteresis branch in the low temperature region for intermediate $D$

If we take the value of  $D$  below  $D_{\text{CG}}$ , we find that a metastable branch appears at low temperatures. In Fig. 8, we display the temperature dependence of  $q$  for  $D = 5.2$  by the bold curve, and the corresponding temperature dependence of the free energy in Fig. 9(a). Here we find that the free energy has a local minimum of HS at low temperatures. This low temperature metastable branch of HS may play an important role for the long-lived metastable state in Co-Fe PBA. In this case, the metastability of HS is intrinsic, and if the initial state is set to be near the metastable point, the value of  $q$  is expected to move first to the metastable value and then relax to the LT state through a nucleation process. However, if there is no metastable branch at low temperatures, as in the case  $D = 6.3$ , the long-lived HS state must be purely due to the slow dynamics. In this case,  $q$  always moves to 0. Checking this initial change of  $q$ , one may find which case is realized. It would be interesting to determine the cases to which individual materials belong.

### 3.3. Small $D$ behavior

If we reduce  $D$  further, e.g., for  $D = 4$ , the HT state becomes metastable at all temperatures, as depicted in Fig. 8 by the thin curve. The free energy change

in this case is plotted in Fig. 9(b). This case corresponds to the dependence found in the CT transition, as shown in Fig. 3. For  $D = 4$ , the high temperature branch connects to the metastable HT branch at low temperatures. This is topologically different from the situation for large values of  $D$ . It should be noted that in this case, the potential barrier between the metastable HT state and the stable LT state exhibits a non-monotonic dependence, and the metastable state readily relaxes to the stable LT state via a nucleation process in the intermediate temperature region. The dependence of the barrier is plotted in Fig. 10.

3.4. *Topological change of the structure of solutions*

To this point, we have found two regions of  $D$ . In the large  $D$  region, the solution of the HT state at high temperatures connects to the LT state at low temperatures. By contrast, in the small  $D$  region,

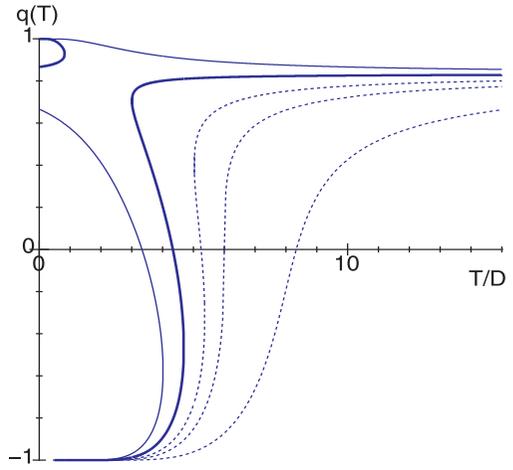


Fig. 8. Temperature dependences of  $q$  for  $D = 5.2$  (bold solid curve) and  $D = 4.0$  (thin solid curve). The dotted curves represent  $q(T)$  for  $D = 10, 7.2,$  and  $6.3$ , which are depicted in Fig. 6. Here,  $J = 1$  and  $\alpha = 1.2$  ( $g = e^{2.4}$ ).

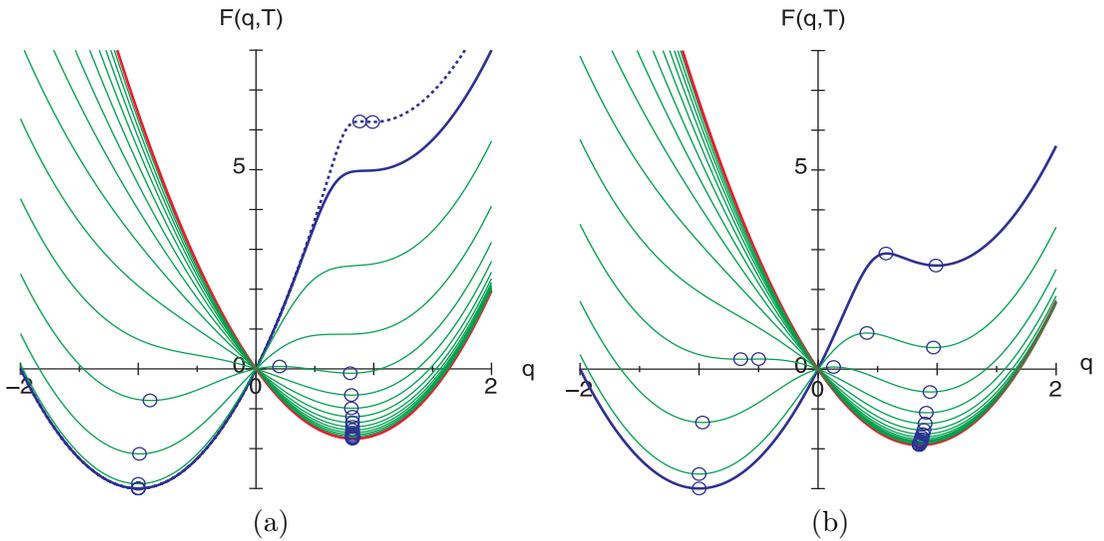


Fig. 9. Temperature dependence of the free energy of functions of  $q$  for (a)  $D = 5.2$  and (b)  $D = 4.0$ . The temperature changes in jumps of 1 from  $T = 15$  (red) to 1 (blue). The data for  $T = 0.5$  are also plotted by the bold dotted blue curves. Here,  $J = 1$  and  $\alpha = 1.2$  ( $g = e^{2.4}$ ).

the solution of the HT state at high temperatures remains until  $T = 0$ . There, a low temperature solution exists separately. Thus, there is a critical value of  $D$  between these two regions. We depict  $q(T)$  at the critical value of  $D$  in Fig. 11. In the mean-field theory,  $q(T)$  does not depend on the temperature at this marginal value of  $D$ . The values of  $q(T)$  and the marginal  $D$  are found in the following analysis. If the relations

$$q = \frac{D}{Jz} \quad \text{and} \quad q = \tanh \alpha \tag{3.9}$$

hold, then from the self-consistent equation (3.5), we find that

$$q = \tanh \left( \frac{Jzq - D}{k_B T} + \alpha \right) \tag{3.10}$$

is always satisfied. From this relation, we find that the critical value of  $D$  is given by

$$D_{\text{CX}} = zJ \tanh \alpha, \tag{3.11}$$

and

$$q = \tanh \alpha. \tag{3.12}$$

Indeed the marginal value of  $D$  is given by

$$D_{\text{CX}} = 6 \times \tanh(1.2)J = 5.00193 \cdots J. \tag{3.13}$$

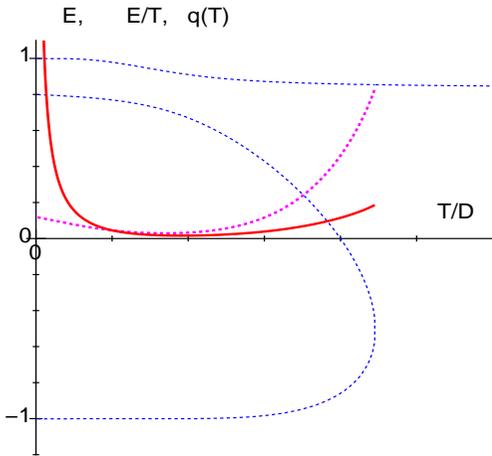


Fig. 10. Temperature dependence of the barrier height between the metastable HT state and the stable LT state for  $D = 4.8$ . The temperature dependence of  $q(T)$  is also plotted by the thin dotted curves. The energy barrier  $\Delta E$  is depicted by the bold dotted curve, and  $\Delta E/k_B T$  is depicted by the bold curve. Here,  $J = 1$  and  $\alpha = 1.2$  ( $g = e^{2.4}$ ).

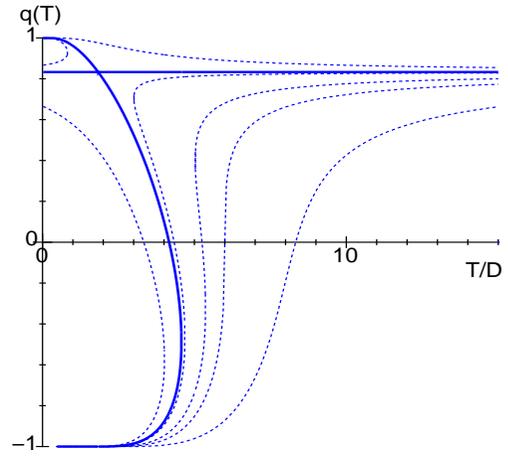


Fig. 11. Temperature dependence of  $q(T)$  for  $D = D_{\text{CX}}$  (solid curve). The temperature dependences for the values studied previously are plotted by the dotted lines ( $D = 10, 7.2, 6.3, 5.2$  and  $4.0$ ). Here,  $J = 1$  and  $\alpha = 1.2$  ( $g = e^{2.4}$ ).

### 3.5. Sequence of the types of structure

Here we found three critical values of  $D$ . Finally, let us point out the fact that the isolated low temperature metastable branch of HS exists for all values of  $\alpha$ . That is, in order to have a metastable state at low temperature,  $D$  must be smaller than  $D_{CG}$ , i.e.,

$$D < zJ, \quad (3.14)$$

and in order to avoid the situation that the solution of HT exists at all temperatures,  $D$  must satisfy the condition

$$D < D_{CX} = zJ \tanh \alpha. \quad (3.15)$$

These conditions are compatible, although the region of  $D$  is rather narrow for large  $\alpha$ . In experiments, one may control the degree of degeneracy by changing the pressure, etc. It would be very interesting to experimentally find the qualitative change of the temperature dependence of metastable states that was found here.

## §4. Summary and discussion

In this paper, we studied models for phase transitions of systems consisting of spin-crossover atoms. We pointed out that the apparently different models for the spin-crossover transition and for the charge-transfer transition are equivalent, and we comprehensively studied structures of stable and metastable states of the unified model. We found several qualitatively different ordering processes, and found critical values of  $D$  between different types of ordering processes. In particular, we found a metastable HS state at low temperatures that exists separately from the high temperature HS state. We found that a metastable HS state exists universally in the present type of model. This metastable HS state at low temperature should play an important role in the pumping process by light-irradiation. We hope that the present study will be useful in classifying the metastability of various photomagnetic materials for which metastability may be investigated by photo-irradiation.

In Co-Fe PBA and CT materials, the system exhibits a magnetic ordering in addition to the spin structure change. In that case, we have to consider the magnetic interaction. Determining the effect of the magnetic interaction on the combined ordering process of the fraction ( $q$ ) of HS and the magnetic order ( $m$ ) is an interesting problem. Here it should be noted that the magnetic state is always metastable, but it is not the equilibrium state unless the magnitude of the interaction is of the order of  $D$  in the models of SC. If  $D$  is so large that the magnetic state appears in equilibrium, then the transition between HS and LS is smooth, and a first-order phase transition does not take place. The detailed properties of the magnetic transition will be reported elsewhere.<sup>36), 37), 65)</sup> This feature of a metastable magnetic state is compatible with the observation in Co-Fe PBA.

In the CT system, however, the magnetic ordered state appears as an equilibrium state at a temperature much lower than the CT transition temperature. In order to explain this magnetic transition, we need to consider the special properties of the CT system. Indeed, in the CT system, magnetic moments exist on B-sites even at low

temperatures. One of the present authors has proposed a mechanism through which the thermal fluctuations of A-sites could mediate the magnetic ordering between B-sites.<sup>62)</sup> However, this mechanism has been found to be unfeasible, at least in two-dimensional systems,<sup>63)</sup> and several alternate possible origins of magnetic ordering are under investigation. In particular, it is possible that quantum fluctuations help the magnetic ordering, e.g., the mixed-valence delocalization mechanism.<sup>66)</sup> A study of this possibility will be reported elsewhere.<sup>64)</sup>

### Acknowledgements

The present work is partially supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology, and also by the NAREGI Nanoscience Project of the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors also thank the Supercomputer Center, Institute for Solid State Physics, University of Tokyo, for the facilities.

### References

- 1) P. Gülich, *Struct. Bonding (Berlin)* **44** (1981), 83.
- 2) P. Gülich, A. Hauser and H. Spiering, *Angew. Chem. Int. Ed.* **33** (1994), 2024.
- 3) O. Kahn, *Molecular Magnetism (VCH, New York, 1993)*.
- 4) G. A. Renovitch and W. A. Baker, *J. Am. Chem. Soc.* **89** (1967), 6377.
- 5) H. Oshio, K. Kitazaki, J. Mishiro, N. Kato, Y. Maeda and Y. Takashima, *J. Chem. Soc. Dalton Trans.* **6** (1987), 1341.
- 6) J. Jeftic, H. Romstedt and A. Hauser, *J. Phys. Chem. Solids* **57** (1996), 1743.
- 7) J. F. Létard, P. Guionneau, E. Codjovi, O. Lavastre, G. Bravic, D. Chasseau and O. Kahn, *J. Am. Chem. Soc.* **119** (1997), 10861.
- 8) J. Jeftic and A. Hauser, *J. Phys. Chem. B* **101** (1997), 10262.
- 9) V. Niel, M. C. Muñoz, A. B. Gasper, A. Galet, G. Levchenko and J. A. Real, *Chem. Eur. J.* **8** (2002), 2446.
- 10) P. Gülich, A. B. Gasper, V. Ksenofontov and Y. Garcia, *J. of Phys: Cond. Mat.* **16** (2004), S1087.
- 11) T. Kambara, *J. Phys. Soc. Jpn.* **50** (1981), 2257.
- 12) S. Decurtins, P. Gülich, K. M. Haselbach, H. Spiering and A. Hauser, *Inorg. Chem.* **24** (1985), 2174.
- 13) A. Hauser, *Chem. Phys. Lett.* **192** (1992), 65.
- 14) J. F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau and O. Kahn, *Inorg. Chem.* **37** (1998), 4432.
- 15) J. F. Létard, J. A. Real, N. Moliner, A. B. Gaspar, L. Capes, O. Cadour and O. Kahn, *J. Am. Chem. Soc.* **121** (1999), 10630.
- 16) F. Renz, H. Spiering, H. A. Goodwin and P. Gülich, *Hyperfine Interact.* **126** (2000), 155.
- 17) Y. Ogawa, T. Ishikawa, S. Koshihara, K. Boukheddaden and F. Varret, *Phys. Rev. B* **66** (2002), 073104.
- 18) T. Tayagaki and K. Tanaka, *Phys. Rev. Lett.* **86** (2001), 2886.
- 19) I. Shteto, K. Boukheddaden and F. Varret, *Phys. Rev. E* **60** (1999), 5139.
- 20) M. Nishino, S. Miyashita and K. Boukheddaden, *J. Chem. Phys.* **118** (2003), 4594.
- 21) M. Nishino, K. Boukheddaden, S. Miyashita and F. Varret, *Phys. Rev. B* **68** (2003), 224402.
- 22) M. Nishino, K. Boukheddaden, S. Miyashita and F. Varret, *Polyhedron* (2005), in press.
- 23) K. Boukheddaden, *Prog. Theor. Phys.* **112** (2004), 205.
- 24) C. P. Slichter and H. G. Drickamer, *J. Chem. Phys.* **56** (1972), 2142.
- 25) R. Zimmermann, *J. Phys. Chem. Solids* **44** (1983), 151.
- 26) T. Kambara, *J. Phys. Soc. Jpn.* **49** (1980), 1806.
- 27) N. Sasaki and T. Kambara, *J. Chem. Phys.* **74** (1981), 3472.
- 28) T. Kambara, *J. Chem. Phys.* **74** (1981), 4557.

- 29) S. Ohnishi and S. Sugano, *J. of Phys. C* **14** (1981), 39.
- 30) H. Spiering, E. Meissner, H. Köppen, E. W. Müller and P. Gülich, *Chem. Phys.* **68** (1982), 65.
- 31) M. Sorai and S. Seki, *J. Phys. Chem. Solids* **35** (1974), 555.
- 32) M. Sorai, *Bull. Chem. Soc. Jpn.* **74** (2001), 2223.
- 33) K. Boukheddaden, I. Shteto, B. Hôo and F. Varret, *Phys. Rev. B* **62** (2000), 14796; *ibid.* **62** (2000), 14806.
- 34) K. Boukheddaden, F. Varret, S. Salunke, J. Linares and E. Coddjovi, *Phase Transitions* **75** (2002), 733.
- 35) K. Boukheddaden, J. Linares, E. Coddjovi, F. Varret, V. Niel and J. A. Real, *J. Appl. Phys.* **93** (2003), 7103.
- 36) K. Boukheddaden, M. Nishino, S. Miyashita and F. Varret, *Phys. Rev. B* **72** (2005), 014467.
- 37) M. Nishino, K. Boukheddaden, S. Miyashita and F. Varret, *Phys. Rev. B* **72** (2005), 064452.
- 38) J. Wajnflasz and R. Pick, *J. Phys. Colloque* **32** (1971), C1.
- 39) K. Nasu, *Relaxations of Excited States and Photo-Induced Structural Phase Transitions* (Springer-Verlag, Berlin, 1997).
- 40) M. Nishino and S. Miyashita, *Phys. Rev. B* **63** (2001), 174404.
- 41) M. Nishino, K. Yamaguchi and S. Miyashita, *Phys. Rev. B* **58** (1998), 9303.
- 42) T. Kawamoto, Y. Asai and S. Abe, *Phys. Rev. B* **60** (1999), 12990.
- 43) A. Ludi and H. U. Güdel, *Struct. Bonding (Berlin)* **14** (1973), 1.
- 44) M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Sculler, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier and F. Villain, *Coord. Chem. Rev.* **190** (1999), 1023.
- 45) T. Mallah, S. Thiébaud, M. Verdaguer and P. Veillet, *Science* **262** (1993), 1554.
- 46) W. R. Entley and S. G. Girolami, *Science* **268** (1995), 397.
- 47) S. Ferlay, T. Mallah, R. Ouahès, P. Veillet and M. Verdaguer, *Nature* **378** (1995), 701.
- 48) W. E. Buschmann, S. C. Paulson, M. C. Wynn, A. M. Girtu, J. A. Epstein, H. S. White and J. S. Miller, *Adv. Mater.* **9** (1997), 645.
- 49) S. Ohkoshi, Y. Abe, A. Fujishima and K. Hashimoto, *Phys. Rev. Lett.* **82** (1999), 1285.
- 50) S. Ohkoshi, K. Arai, Y. Sato and K. Hashimoto, *Nature Materials* **3** (2004), 857.
- 51) S. Ohkoshi and K. Hashimoto, *J. Photochem. Photobiol. C* **2** (2001), 71.
- 52) O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science* **272** (1996), 704.
- 53) O. Sato, Y. Einaga, T. Iyoda, A. Fujishima and K. Hashimoto, *J. Electrochem. Soc.* **144** (1997), L11.
- 54) G. Champion, V. Escax, C. C. Moulin, A. Bleuzen, F. Villain, F. Baudalet, E. Dartyge and M. Verdaguer, *J. Am. Chem. Soc.* **123** (2001), 12544.
- 55) N. Shimamoto, S. Ohkoshi, O. Sato and K. Hashimoto, *Inorg. Chem.* **41** (2002), 678.
- 56) S. Ohkoshi, S. Yorozu, O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Appl. Phys. Lett.* **70** (1997), 1040.
- 57) S. Ohkoshi, Y. Einaga, A. Fujishima and K. Hashimoto, *J. Electroana. Chem.* **473** (1999), 245.
- 58) H. Tokoro, S. Ohkoshi and K. Hashimoto, *Appl. Phys. Lett.* **82** (2003), 1245.
- 59) F. Varret, A. Goujon, K. Boukheddaden, M. Mognès, A. Bleuzen and M. Verdaguer, *Mol. Cryst. Liq. Cryst.* **379** (2002), 333.
- 60) N. Kojima, W. Aoki, M. Itoi, Y. Ono, M. Seto, Y. Kobayashi and Y. Maeda, *Solid State Commun.* **120** (2001), 165.
- 61) N. Kojima, W. Aoki, M. Seto, Y. Kobayashi and Y. Maeda, *Synth. Met.* **121** (2001), 1796.
- 62) S. Miyashita and N. Kojima, *Prog. Theor. Phys.* **109** (2003), 729.
- 63) Y. Konishi and S. Miyashita, *J. Phys. Soc. Jpn.* **74** (2005), Suppl. p. 103.
- 64) Y. Konishi and S. Miyashita, in preparation.
- 65) M. Nishino, K. Boukheddaden, F. Varret, Y. Konishi, H. Tokoro and S. Miyashita, in preparation.
- 66) B. Mayoh and P. Day, *J. Chem. Soc. Dalton* **8** (1974), 846.