Abstract.

We investigate time evolution of the magnetization and high spin fraction of the system in which spin-crossover phenomena and magnetic transitions are involved, proposing a new model which allows us to describe both spin-crossover (SC) transition and magnetic ordering of Prussian blue analogs under photolysis. Both the intermolecular lattice interaction and the intermolecular magnetic interaction are considered in this model, which enables unified descriptions of the photoinduced SC transition and magnetic transitions. For the dynamics of the system, we take into account the multi-time scales in a master equation approach for the magnetic relaxation, the lattice (electronic) relaxation, and the photoexcitation process. We observe non-linear dependence of the growth of the magnetization and high spin fraction on irradiation time and that on the strength of irradiation, which are typical properties of SC and PBA compounds. We also observe irreversible magnetization process in a temperature cycle, which reproduces qualitatively well the novel behavior observed in the corresponding experiments.

1. Introduction

Photoinduced phase transitions (PIPT) have currently attracted much interest because they may offer the possibility to build optical memory devices etc. The dynamical properties of PIPT are also important from the viewpoint of the analysis of relaxation phenomena. Lightinduced non-equilibrium dynamics of molecular metal complex solids is an area of intense study for reversible control of magnetic, electronic, structural properties, etc. in bistable systems. Molecular Spin-crossover (SC) solids and Prussian Blue analogs (PBA) are typical materials that exhibit such properties[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15].

The discovery of LIESST (light-induced excited spin state trapping) [1, 4] has led to a number of studies concerning relaxation during and after irradiation. Co-Fe Prussian blue
analogue (PBA) [5] shows the transition between the nonmagnetic state (LS) and the ferrimagnetic ordered state (HS) by photoirradiation: Fe$^{II}(S=0) + Co^{III}(S=0) \rightarrow Fe^{II}(S=1/2) + Co^{III}(S=3/2)$. Recent experiments of PBA have shown that the HS fraction and magnetization after photoirradiation change drastically depending on the temperature cycling processes[10, 11, 12]. There irreversible magnetization process between the warming and cooling processes were found. Motivated by these experiments, we will give a method of dynamics for SC systems with the photoinduced magnetism.

Many studies have clarified that SC transition between the low spin (LS, diamagnetic) and the high spin state (HS, paramagnetic) is not a simple transition of the electronic state of a molecule, but a cooperative transition in correlated molecules. The model proposed by Wajnflasz and Pick (WP-model) [16, 17] in which not only cooperativity but also entropy effect between LS and HS are taken into account, and extended WP-models have explained successfully the static and dynamical properties for spin-crossover transition between the two phases[18, 19, 20, 21, 22, 23].

The self-accelerated relaxation of HS fraction after irradiation is a characteristic of the dynamics of SC compounds. WP-model with Arrhenius dynamics [19] has successfully reproduced the behavior. For reversible switching of magnetization, the Blume-Capel (BC) model[24, 25], which has a long-lived metastable ferromagnetic state in a parameter region, was studied. There, the dynamical process of the two-way switching was investigated focusing on the magnetic interaction and the multi-time scales of microscopic dynamics[26, 27].

Very recently we have proposed a unified model in which both the inter-molecular lattice interaction and the inter-molecular magnetic interaction are taken into account and investigated static and dynamical properties of the model[28, 29]. This generalized model includes both the WP and BC models as special cases.

Here, using the generalize model, we will demonstrate the typical shapes of the increase of the magnetization as well as the HS fraction during photoirradiation at low temperatures and find that these are realized as non-linear functions of irradiation time, which qualitatively agrees with the experimental data[10, 30]. Experimentally, it has been observed that the HS fraction and magnetization change drastically depending on the temperature cycling processes[10, 11, 12]. We will reproduce the irreversible magnetization of the cycling process and consider the origin of the difference of the transition temperatures of magnetization between the warming process and cooling process.

2. Methods

We adopt a model describing both the magnetic and elastic interactions in the form [28, 29]:

$$
H = -J \sum_{\langle i,j \rangle} S_i S_j - K \sum_{\langle i,j \rangle} (S_i^2 - \frac{1}{2}) (S_j^2 - \frac{1}{2}) + (D - \frac{\ln g}{\beta}) \sum_i (S_i^2 - \frac{1}{2}) - h \sum_i S_i, \quad S_i = 0, 1, -1, (1)
$$

where 0 denotes nonmagnetic state (LS state) and 1 and −1 denote up spin and down spin states (HS state), respectively. Here, $g(= \frac{1}{\mathcal{N}})$ is the effective degeneracy ratio between the HS and LS states [19] (the $u$-fold LS state and the $r$-fold up spin (down spin) HS state). $J$ is the magnetic interaction, $D(> 0)$ is the ligand-field energy, $g$ is the effective degeneracy ratio between the HS and LS states [19], $\beta = \frac{1}{k_B T}$, and $h$ is the magnetic field. $K(> 0)$ denotes the inter-molecular interaction which originates in the elastic interaction. This simplified interaction means that an attractive force acts for the same state (LS-LS or HS-HS), which leads to the bistable nature of SC compounds. If we take $K = 0$ and $g = 1$, it corresponds to BC model. If we introduce $\sigma_i = 2S_i^2 - 1$ with $J = 0$, it reduces to WP model: $H = -\frac{4J}{K} \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \frac{1}{2} \left( D - \frac{\ln 2g}{\beta} \right) \sum_i \sigma_i$.

Although PBA has a sub-lattice structure and a ferrimagnetic state, we consider a simple cubic lattice with the nearest-neighbor (i, j) interaction and take ferromagnetic coupling ($J > 0$) for simplicity. The parameters are set as $J = 5K$, $K = 300K$, $D = 1200K$ which give realistic
values of transition temperatures for PBA compounds[10, 11, 12]. The ratio $g$, which depends on the degree of freedom of spin, orbital, and lattice and molecular vibrations, increases up to 100 – 1000, and temperature dependent [19]. In the present work, we take $g$ as constant ($g = 200$) for simplicity.

Stochastic dynamics described by the following master equation is used for the dynamics of the model:

$$\frac{d}{dt} P(S_1 \cdots S_k \cdots S_N, t) = \hat{L}(t) P(S_1 \cdots S_k \cdots S_N, t). \quad (2)$$

In eq. (2), $P$ is the probability of the state $\{S_1 \cdots S_k \cdots S_N\}$ at time $t$ and $\hat{L}(t)$ denotes the time evolution operator. The transition probabilities such as $W_k(S_k \rightarrow S'_k)$ for the $k$-th site compose $\hat{L}(t)$. Here, the variable $S_k(S'_k)$ takes a value 0, 1, or $-1$.

Here, we adopt the dynamics with multi time scales to describe different relaxation processes for the dynamics of the magnetization and HS fractions[27]. Because the transition between LS and HS states ($S = 0$ and $|S| = 1$) is accompanied by structural change, the time scale of this process is considered to be much slower than that of spin inversion ($S = \pm 1$). We use Arrhenius dynamics[19] for the HS $\leftrightarrow$ LS flip process and standard Glauber type evolution between $S = 1$ and $S = -1$ for the spin flip process.

We can construct the following time evolution including the process of photoirradiation[27],

$$\hat{L}(t) = p_{\text{latt}} \hat{L}_{\text{latt}}(t) + p_{\text{spin}} \hat{L}_{\text{spin}}(t) + p_{\text{photo}} \hat{L}_{\text{photo}}(t). \quad (3)$$

Here, $\hat{L}_{\text{latt}}$, $\hat{L}_{\text{spin}}$, and $\hat{L}_{\text{photo}}$ denote the process of LS-HS transition, spin flip transition and the photoexcitation process, respectively.

The transition probability of Arrhenius dynamics is given by $W_k^{\text{latt}}(S_k \rightarrow S'_k) = \frac{1}{2} \exp(-\beta(E_0 - E(S_k)))$, where $S_k$ is 0 ($\pm 1$) and $S'_k$ is $\pm 1$ (0), and $E(S_k)$ is a local energy of eq. (1). The quantity $E_0 - E(S_k)$ represents the effective energy barrier between initial ($S_k$) and final ($S'_k$) states and $E_0$ is set as $E_0 = 1000K$[19, 22]. This transition probability is used for $\hat{L}_{\text{latt}}$. The transition probability of Glauber dynamics is given by $W_k^{\text{spin}}(S_k \rightarrow S'_k) = \frac{1}{2}(1 - S_k \tanh \beta \Delta E)$, where $S_k = 1$ ($-1$) and $S'_k = -1(1)$ and $\Delta E = J \sum_{i \neq k} S_i$. This transition probability is used for $\hat{L}_{\text{spin}}$.

The irradiation process of LS $\rightarrow$ HS, which is assumed to be a local phenomenon, following the experimental data [10], is expressed as $S_k = 0 \rightarrow S'_k = \pm 1$ with the same probability, i.e., $W_k^{\text{photo}}(0 \rightarrow \pm 1) = \frac{1}{2}$. The three processes are schematically shown in figure 1.

Here, the coefficients are related to relative strength[27] for each process and we adopt $p_{\text{latt}} + p_{\text{spin}} + p_{\text{photo}} = 1$. We take $p_{\text{latt}}/p_{\text{spin}} = 1$. Other choices do not change the relaxation dynamics here qualitatively. We focus on the following order parameters: the magnetization

$$m = \langle (\sum_i S_i)^2 \rangle / N^2 \quad (4)$$

and high spin fraction

$$q = \langle \sum_i S_i^2 \rangle / N. \quad (5)$$

Here, $N$ is the system size (set as $N = 20^3$) and $\langle \rangle$ is an average over a stochastic process.

First, the system is irradiated at a very low temperature ($T_0 = 5K$) under a magnetic field ($h = 0.1$). We observe the following cases: $p_{\text{photo}} = 0.01$, 0.02, and 0.03. After the state becomes the saturated magnetic HS state ($q = 1$ and $m = 1$), we switch off the irradiation and applied field (setting $p_{\text{photo}} = 0$ and $h = 0$). Then, we change the temperature. The temperature is gradually changed in 1 K steps (1000 Monte Carlo steps (MCS) for the transient time and
another 1000MCS for measuring) and it is increased up to $T_{\text{max}} = 90K$. Then it is decreased to the initial temperature $T_0$ (i.e., $T_0 \rightarrow T_{\text{max}} \rightarrow T_0$). Here we observe the magnetization and HS fraction as functions of time (temperature).

Figure 1. Schematic view of the transition probabilities between the LS ($S = 0$) and the HS ($S = \pm 1$) states. $W_{\text{spin}}, W_{\text{latt}}, W_{\text{photo}}$ correspond to the spin, lattice, and irradiation probabilities, respectively.

Figure 2. Time dependence of $m$ under photoirradiation. $p_{\text{photo}} = 0.001(+)\,$, $0.002(\times)$, and $0.003(\ast)$.

3. Results

In figure 2, we show the time evolution of magnetization ($m$) under photoirradiation. The parameters of the strength of irradiation were taken as $p_{\text{photo}} = 0.01, 0.02,$ and $0.03$. The time evolution of the HS fraction ($q$) exhibited similar time dependence (not shown here) although the magnetization has a little bit time delay of the growth of $q$ and it follows the change of $q$. This is due to the fact that the magnetic interactions acts between the magnetic moments of the HS sites which were excited by photoirradiation and the magnetic moments align in the direction of the magnetic field. All time dependences of the magnetization $m$ have characteristic features. All $m$ increase slowly with concave shapes at the beginning of the increase and they are accelerated in the middle region and at the end of the increase they saturate slowly with convex shapes. These time dependences are consistent with the experiments[10, 30]. We found not only non-linear time dependence of $m$ (and $q$) but also non-linear irradiation-strength dependence of $m$ (and $q$). We changed the relative strength of irradiation as twice, three times but the speeds of the increase of $m$, the initial points of acceleration, the saturated points, etc., were found to have no simple relations between the different strengths. These features were also seen in all $q$.

We can suggest the following. At the beginning of the photoirradiation, the irradiation makes local excited HS states but almost all sites are in the LS state and HS sites easily change back to the LS state due to the cooperative effect. Thus the growth of $m$ (and $q$) is suppressed and it leads to the concave dependence. However, when the number of HS sites is increased, the cooperative effect between HS sites becomes more significant. The cooperative effect here helps
the growth of $m$ (and $q$). Then it results in the acceleration of $m$ (and $q$). Finally, the reduction of LS sites, which are candidates to change HS sites, leads to decelerate of the ratio of $m$ with time. The cooperative effect has non-trivial relation to the strength of the irradiation.

In figure 3, the time (temperature) dependence of $m$ (solid line) and that of $q$ (dashed line) are depicted. We see the different magnetic transition temperatures between the warming process (say $T_C \simeq 23$ K) and the cooling process (say $T'_C \simeq 21$ K). We see $T_C > T'_C$. Here $T_C$ corresponds to the Curie temperature (= $4.5 J = 22.5$ K), which is the critical magnetic transition temperature of 3D Ising model, if we fix the state of all HS sites (i.e., $q = 1$).

Due to the metastability of $q$ which comes from Arrhenius dynamics[29], $q$ does not change at the beginning. Before arriving at $T_{\text{max}} = 90$ K in the warming process, the HS fraction $q$ begins to reduce and at the beginning of the cooling process the reduction continues until $T \simeq 60$ K. However, when the system is cooled more, the reduction of $q$ stopped and the value of $q$ does not change during the cooling process afterwards. The state of $q$ becomes like a frozen state with $q < 1$. This state is realized as a diluted HS states and the magnetic interaction $J$ acts within the diluted sites. Thus the reduction of the critical temperature of magnetization occurs. Indeed reductions of the transition temperature in temperature cycles were observed in the experiments[10, 11] and our results reproduce the experimental results qualitatively.

![Figure 3](image.png)

**Figure 3.** Temperature (time) dependence of $m$ (solid line) and that of $q$ (dashed line).

4. Summary
We have presented a formulation which allows us to describe dynamical properties of PBA including the effect of photoirradiation, more generally, dynamics of SC compounds with magnetic ordering. We employed stochastic dynamics of the system with multi-time scales: Arrhenius dynamics for LS-HS transition, Glauber dynamics for spin transitions, and local excitations for the effect of photoirradiation. We observed temperature (time) dependence of magnetization ($m$) and high spin fraction ($q$) of the system. We considered not only the lattice interaction which induces LS-HS transitions but also the magnetic interaction which leads to magnetic ordering, and presented the non-linear dependence of the growth of $m$ (and $q$) on irradiation time and that on the strength of the irradiation, which are typical properties of SC and PBA compounds.
In the temperature cycle, the second-order magnetic transition takes place at the Curie temperature \( T_C \simeq 22.5K \) in the warming process staring from the saturated HS and magnetic state \((m = 1\text{ and } q = 1)\) by photoirradiation. However, the reduction of the magnetic transition temperature was observed \((T_C > T_C')\) in the cooling process. The reduction of \(q\) results in a diluted lattice, which causes the reduction of the magnetic transition temperature in the warming process. Our method reproduced the irreversible process of magnetic ordering qualitatively which was observed in the experiments[10, 11]. Thus, our methodology for the dynamics of the generalized model will catch the essence of the dynamics of PBA.

Acknowledgements
The present work was supported by Grant-in-Aid for Scientific Research from MEXT of Japan, and Ministère de l’Education Nationale and CNRS (PICS France-Japan Program) of France. The authors are grateful for financial support from the Grants. The numerical calculation is supported by the supercomputer center of ISSP of Tokyo university.

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