Dynamical Aspects of the Photoinduced Phase Transition in Spin-Crossover Complexes

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We report a dynamical study on the photoinduced cooperative changes of the spin configurations in single crystals of the organometal spin-crossover complex. In the photoswitching process between low- and high-spin states, nonlinear characteristics such as thresholdlike behavior, incubation period, and phase separation have been observed. These results demonstrate that the cooperative intersystem crossing mediated by spin-lattice interaction plays a key role in the driving process of a new class of nonequilibrium phenomena so called photoinduced phase transition.

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Systems that show changes in chromic, magnetic, dielectric, and transport properties by light irradiation with high sensitivity are an attractive target for materials science. One important strategy for developing highly responsive photoexcitation materials is to identify the photocontrol of the cooperative phenomena. This exotic photoeffect, called a photoinduced domino effect, can also be named a photoinduced phase transition (PIPT). Recently, extensive studies have been started in search for materials which show PIPT phenomena [1]. However, the dynamical and nonlinear natures of PIPT have been scarcely reported though they are important targets for the field of nonequilibrium and nonlinear dynamics.

Among various candidates for PIPT, organometal spin-crossover complex is an attractive one. For example, an octahedral transition metal complex with six d electrons can adopt a high-spin (HS) configuration ($^5T_2; t_{2g}^4 e_g^2$) with a total spin (S) of 2 and a low-spin (LS) configuration ($^1A_1; t_{2g}^6$) with $S = 0$ according to the strength of the ligand field (see Fig. 1) [2]. A cooperative change in the spin configuration, called a spin state phase transition, may be induced by photoexcitation in this class of materials, if the constituent metal-ligand complexes are structurally combined with each other.

In an organometal complex $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ (2-pic = 2−aminomethyl-pyridine) (hereafter abbreviated as Fe-pic), Fe^{2+} ion and six nitrogen atoms of three 2-pic molecules construct the octahedral metal-ligand complex, and every constituent unit is combined with three other ones around it via hydrogen bonds (see Fig. 1) [3]. Indeed, the cooperative spin-lattice interaction really induces the first order and two-stage phase transition at critical temperatures (T_c's) of 121 and 114 K [2]. In addition, the occurrence of bidirectional phototransformation between LS and HS states, named light-induced excited spin state trapping, was reported for this crystal [2,4]. Based on these characteristics, the Fe-pic crystal can be classified as

an important target not only for the search of a new class of PIPT, but also for the study of the dynamical process of it.

In this Letter, we demonstrate that the efficiency of the photoconversion from LS to HS states in Fe-pic crystals and the conversion process itself show a thresholdlike behavior depending on the excitation intensity. In addition, the dynamical study of this photoconversion process makes
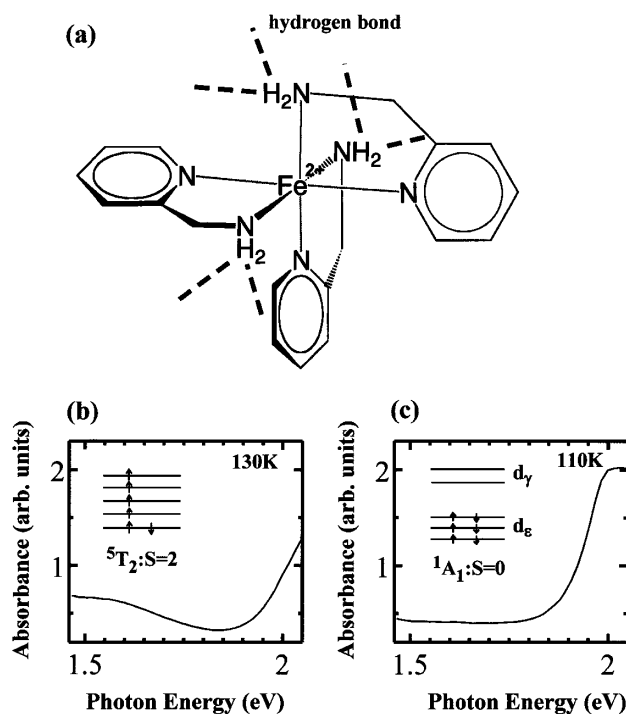

FIG. 1. (a) Schematic structure of $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$. Metal-ligand complexes are combined via hydrogen bonds, as indicated by the dashed line. (b),(c) Absorption spectra and schematic spin configurations in high-spin and low-spin states, observed at 130 K ($>T_c$) and 110 K ($<T_c$), respectively.

clear the existence of an incubation period and the occurrence of phase separation. Based on the obtained results, a new class of PIPT mediated by spin-lattice interaction is identified and the dynamical natures of it are clearly characterized.

To probe the photoconversion process in Fe-pic crystals, a spectroscopic measurement was employed as well as magnetization measurement. This is because the energy positions of the absorption bands due to d-d transitions of Fe^{2+} ions are highly sensitive to the spin configuration which is visually illustrated in Fig. 1. In the HS (LS) phase, absorption band attributed to $^5T_2 \to {}^5E$ ($^1A_1 \to {}^1T_1$) can be observed at 1.5 (2.0) eV as shown in Fig. 1(b) [Fig. 1(c)] [5]. Therefore, the fraction of the LS (HS) state denoted by χ ($1 - \chi$) can be probed by the absorption intensity observed at 1.5 (1.9) eV. The dynamical changes in χ (dependence on time τ) observed at 2.2 K under continuous irradiation of 1.8 eV light with various intensities estimated by spectroscopic and

magnetic measurements are plotted in Figs. 2(a) and 2(b), respectively [6]. In these figures, the crystal was originally in the LS state ($\chi = 1$), and light irradiation started at $\tau = 0$ s. Typical sizes of the crystals utilized for optical and magnetic measurements were $0.5 \times 0.5 \times 0.05$ mm^3 and $1.5 \times 1.5 \times 0.1$ mm^3, respectively.

The first notable point in these figures is that the efficiency of the photoconversion strongly depends on the excitation photon flux (I). Hereafter, I (photon cm^{-3} s^{-1}) denotes the photon number absorbed by a fraction of the crystal with one cubic centimeter for every second and is abbreviated as cm^{-3} s^{-1}. The occurrence of LS $\to$ HS phototransformation was not observed if the value of I was smaller than 9.0×10^{-17} cm^{-3} s^{-1} (I_{th}) as shown in Fig. 2(a). Similar thresholdlike behavior was confirmed by magnetic measurement. In addition, the threshold behavior was also observed when we measured the I dependence of the converted HS fraction while keeping the totally absorbed photon number ($N_{tot} = I$ [cm^{-3} s^{-1}] $\times \tau$ [s]) at a constant value ($N_{tot} = 5.7 \times 10^{20}$ cm^{-3}) [see inset in Fig. 2(b)]. This clearly indicates that the converted fraction strongly depends on I rather than N_{tot}.

The observed lifetime of the photoinjected HS phase was longer than 10^4 s. Furthermore, the occurrence of the photoconversion from HS (high-temperature) to LS (low-temperature) states was confirmed by spectroscopic measurement. The photoconverted HS crystal, which was prepared by 1.8 eV light irradiation went back to the original LS phase by 1.5 eV light irradiation and the photoconversion efficiency also strongly depended on the I value [4,7]. The estimated threshold value (I_{th}) for HS $\to$ LS conversion was 3×10^{18} cm^{-3} s^{-1}. These results indicate that the observed photoconversion and thresholdlike behavior cannot be attributed to the effect of the heating of the crystals by light irradiation beyond T_c. In addition, the photoexcitation resonant to the d-d transition can more efficiently drive the cooperative change in spin state than other electronic excitation bands. It also supports the idea that the observed photoconversion is triggered really via photon mode and spin-lattice interaction plays a key role to drive PIPT in Fe-pic.

The second characteristic in Fig. 2 is the existence of an incubation period (τ_{incu}) analogous to martensitic transformation [8]. The large and abrupt increase of the conversion speed was observed when the HS fraction ($1 - \chi$) exceeded $(7 \pm 3)\%$ though the excitation intensity I ($> I_{th}$) was kept constant [see dashed and dash-dotted lines in Fig. 2(a)]. Here the period between the beginning of the photoexcitation and the abrupt enhancement in the photoconversion speed is called as τ_{incu} as shown in Fig. 2(a). A similar behavior was confirmed even when changing the value of I to various degrees. Of course, τ_{incu} changed according to the I value because the interval for accumulating 7% HS in host LS crystal depended on I. These results indicate that the photodoping of the HS state of $(7 \pm 3)\%$ into the host LS crystal dramatically
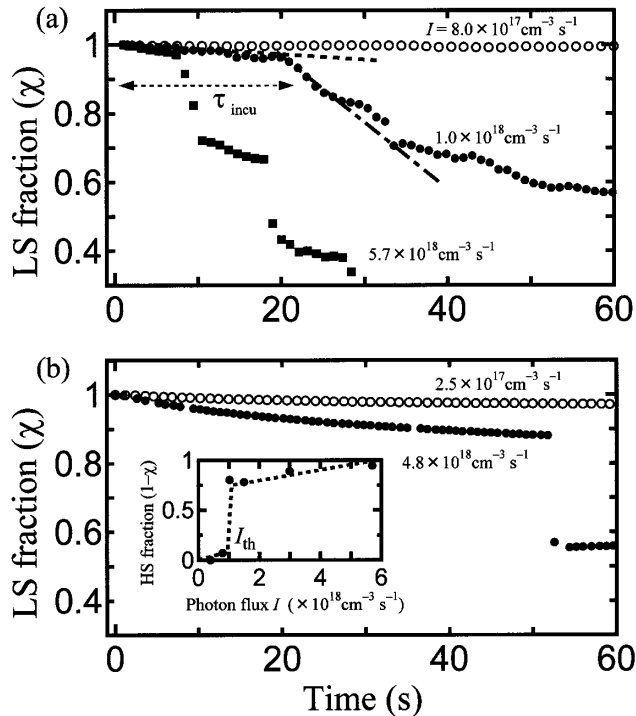

FIG. 2. Dynamical process of the photoconversion from LS to HS states at 2.2 K. The χ values plotted in (a) have been estimated based on absorption. Open circles, filled circles, and filled squares are for excitation photon flux (I) of 8.0×10^{17}, 1.0×10^{18}, and 5.7×10^{18} cm^{-3} s^{-1}, respectively. The average photoconversion speeds observed at $\tau < \tau_{incu}$ and just after τ_{incu} with $I = 1.0 \times 10^{18}$ cm^{-3} s^{-1} are indicated by inclinations of dashed and dash-dotted lines, respectively. The dynamical changes in χ for $I = 2.5 \times 10^{17}$ and 4.8×10^{18} cm^{-3} s^{-1} probed by magnetic measurement at 10 K are shown in (b) by open and filled circles, respectively. The I dependence of the converted HS fraction ($1 - \chi$), keeping N_{tot} at constant value (5.7×10^{20} cm^{-3}), is plotted in the inset in (b). The threshold value of I for driving the transition is indicated by I_{th}.

changes the photoconversion dynamics. In the case of the HS → LS conversion (reverse direction), similar τ_{incu} was observed though it was not so conspicuous as the case of LS → HS conversion.

The observed exotic behavior was not due to the inhomogeneous and localized excitation of the crystal surface. To homogeneously excite the whole crystals, we carefully tuned the excitation photon energy. As a result, less than 2.5% of the excitation light was absorbed by crystal under the present excitation condition. Rigorously speaking, the light excitation in the case of magnetic measurement is not so homogeneous as in spectroscopic measurement due to the difference in the experimental setup for light excitation [6]. As shown in Fig. 2, the length of τ_{incu} estimated by the former method was longer than that by the latter one even though the similar excitation photon flux was used. We consider that this discrepancy is due to the difference in the photoexcitation condition.

It should be noted that the LS → HS photoconversion process is highly efficient. For example, in the case of 1.0×10^{18} cm^{-3} s^{-1} excitation, an average of 0.19% of Fe^{2+} ions in the crystal ($= 2.9 \times 10^{18}$ ions cm^{-3}) was converted from LS to HS for every second at $\tau < \tau_{incu}$ [dashed line in Fig. 2(a)]. Therefore, the conversion efficiency Φ (i.e., the number of photoconverted Fe^{2+} ions by one absorbed excitation photon) at $\tau < \tau_{incu}$ can be estimated to be $2.9 \times 10^{18}/(1 \times 10^{18}) = 2.9$. Immediately after τ_{incu}, the average conversion speed and Φ abruptly increased to 3.4×10^{19} ions s^{-1} [dash-dotted line in Fig. 2(a)], and 34, respectively. Here, I was held at the same value before and after τ_{incu}. The large value of Φ at $\tau > \tau_{incu}$ is an important characteristic of PIPT phenomena [1].

In addition to these distinguishing traits, the steplike change in the converted fraction is an another important characteristic of the photoconversion process. The steplike behavior has been observed for various crystals and it was conspicuous with rather strong photoexcitation as shown in Fig. 2. The steplike decrease of χ has been confirmed by both spectroscopic and magnetic measurements [Figs. 2(a) and 2(b)], and thus such a behavior is not due to artifacts such as cracks in the crystal. The observed steplike changes suggest the occurrence of the photoinduced phase separation in Fe-pic crystals. To make more investigation on this point, we directly observed the growth of the HS domains at 6.4 K. Dark red-yellow and yellow parts in Fig. 3 show the domains of LS and HS, respectively. At $\tau < \tau_{incu}$, no color change was observed except for slight bleaching [Fig. 3(a)]. When τ reached τ_{incu}, a part of the crystal changed from LS to HS abruptly though the crystal was homogeneously excited [see the region surrounded by the dashed line in Fig. 3(b)]. As τ increased, other HS domains appeared side by side, and finally almost the whole crystal was converted into the HS state. These results clearly indicate the occurrence of the phase separation induced by light irradiation in Fe-pic crystals.
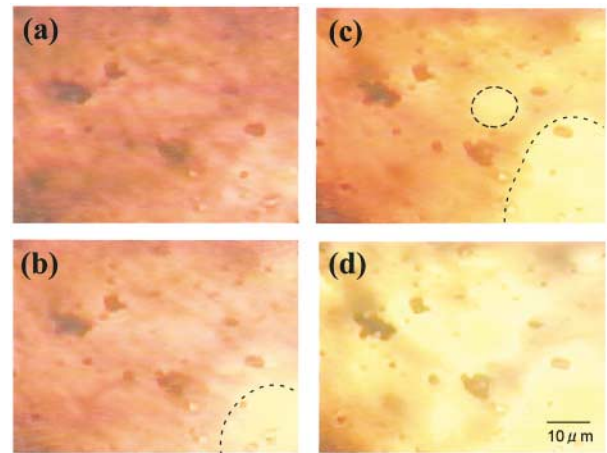

FIG. 3 (color). Transparent photographs of the Fe-pic crystal at 6.4 K under continuous irradiation of 1.9 eV excitation light with $I = 4.0 \times 10^{18}$ cm^{-3} s^{-1} observed by an optical microscope. The sizes of viewgraphs and spatial resolution were 67 μm $\times$ 60 μm and 1 μm, respectively. Viewgraphs of (a), (b), (c), and (d) were observed at $\tau = 0.8\tau_{incu}$, τ_{incu}, $1.3\tau_{incu}$, and $1.7\tau_{incu}$, respectively.

The polarization of the excitation light was not effective for the dynamics of the photoconversion, because the energy positions and intensities of the broad absorption bands due to d-d transition in Fe-pic crystals scarcely depended on the polarization of the light.

Obtained results lead us to the idea that a new class of PIPT occurs in Fe-pic crystals and the cooperative spin-lattice interaction plays a key role in the dynamical process of it. A model calculation based on a simple Hamiltonian also supports this idea [9]. For the treatment of the Fe-pic system, we introduce a simple model where a single site Hamiltonian for the jth component is given by the following equation:

$$H_j = \epsilon_1(u_j)|1\rangle_{jj}\langle 1| + \epsilon_2(u_j)|2\rangle_{jj}\langle 2| + t|1\rangle_{jj} \times \langle 2| + t|2\rangle_{jj}\langle 1|, \qquad (1)$$

where $|1\rangle_j$, $|2\rangle_j$, and u_j are the HS and LS states and the totally symmetric normal coordinate which strongly couples to these electronic states. Here $\epsilon_1(u_j) = (u_j - 2)^2 + \epsilon$ and $\epsilon_2(u_j) = u_j{}^2$ represent the potentials for u_j in HS and LS states, respectively. t gives the coupling between HS and LS. We assume that the interaction among the constituent complexes is brought about by elastic interaction [10], which can be given based on a mean-field-like approximation as $H^{int} = \sum_{i>j}(k/N)(u_i - u_j)^2$, where k denotes the strength of the interaction and N is the total number of the constituent complex. The total Hamiltonian is given by $H = \sum_j H_j + H^{int}$.

The LS → HS transition is triggered by the photoexcitation process (PEX), which is followed by the transitions of the adjacent complexes, using the relaxation energy released by the photoexcited complex. Thus, the LS → HS transition rate is proportional to the photon flux I and the
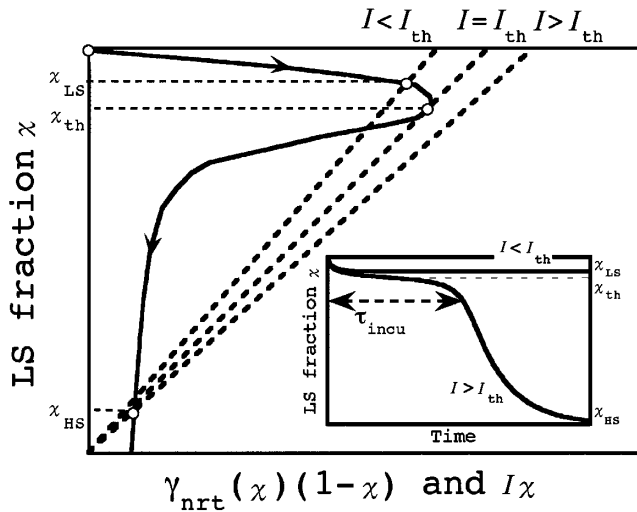
FIG. 4. Stationary solutions of Eq. (3) in case of $m = 1$, which are the intersections of $\gamma_{\text{nrt}}(\chi)(1 - \chi)$ (solid curve) and $I\chi$ (broken lines). At a critical excitation rate (I_{th}), the stationary solution jumps from the LS-dominant solution χ_{LS} to the HS-dominant solution χ_{HS}. The inset shows temporal behavior of the LS fraction for $I < I_{\text{th}}$ (solid curve) and $I > I_{\text{th}}$ (broken curve). χ_{th} is the stationary value of χ at $I = I_{\text{th}}$.

average number m of the spin-converted complexes by one photon. The HS $\rightarrow$ LS transition occurs through a multiphonon nonradiative transition (nrt) of which rate (γ_{nrt}) is sensitive to the LS fraction χ. The altered diabatic potentials are given by $\tilde{\epsilon}_{1,2}(u_j; \chi) = \epsilon_{1,2}(u_j) + k[u_j^2 + 4(1 - \chi)u_j]$, and the energy difference between the potential minima is given by $\Delta\epsilon(\chi) = \epsilon + 4k(2\chi - 1)/(1 + k)$, which implies that the potential barrier for the HS $\rightarrow$ LS decay becomes higher as the HS fraction increases, and thus the HS state is more stabilized. The rate γ_{nrt} at zero temperature is given by Fermi's golden rule:

$$\gamma_{\text{nrt}}(\chi) = 2\pi S^2 t^2 \frac{(4\pi)^n}{\Gamma(n + 1)} \exp(-4S), \qquad (2)$$

where S is the Huang-Rhys factor and $n = n(\chi) = S\Delta\epsilon(\chi)$ is the averaged phonon number released on the transition.

Taking PEX and nrt processes into account, the temporal evolution of the LS fraction $\chi(\tau)$ is governed by the following equation [11]:

$$\frac{d\chi(\tau)}{d\tau} = -mI\chi + (1 - \chi)\gamma_{\text{nrt}}(\chi), \qquad (3)$$

with the initial condition $\chi(0) = 1$. The solution of Eq. (3) is shown in the inset in Fig. 4. The figure indicates the existence of a critical excitation flux (I_{th}) to drive the conversion from LS to HS states. Above I_{th}, following the incubation period τ_{incu}, the HS fraction suddenly increases and finally reaches the HS-dominant stationary

fraction χ_{HS} (see the inset in Fig. 4). In the presence of strong interaction k, the stationary solution jumps at I_{th} from χ_{LS} ($I < I_{\text{th}}$) to χ_{HS} ($I > I_{\text{th}}$) as shown in Fig. 4. The simple model used here could describe the main features of PIPT qualitatively. However, to give spatial or dimensional predictions such as the phase separation, more rigorous treatment including the spatial dependence of interaction k is important.

In this Letter, we have identified PIPT in Fe-pic crystals and characterized the dynamics of it. The characteristic behavior of PIPT is an important subject for the study of cooperative phenomena under nonequilibrium conditions. In addition, the dynamical study of PIPT is essential for understanding the optical switching process of the memory and liquid crystals [1].

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