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Electronic and Structural Phase Transition Controlled by Photo-excitation and Magnetic Field in Spin Crossover Complex

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We report the magnetic field effect on the cooperative photo-induced spin state transition process between low-spin (LS) and high-spin (HS) states in a spin-crossover complex. When the magnetic field is enhanced from 0.5 to 7 T, the transition temperature scarcely decreases only by about 0.2 K. In contrast photo-conversion efficiency from LS to HS state and the relaxation time of photo-converted HS state have been enhanced 7.1 and 1.5 times, respectively.

Keywords: photo-induced phase transition; spin-crossover complex

INTRODUCTION

It is well known that changes in external conditions such as temperature, pressure and magnetic field induce macroscopic phase transition. One of important targets for materials science is to find and develop a system which shows the macroscopic and huge response to photo-excitation. Recently, a few systems in which weak photo-irradiation can trigger the phase transition have been discovered. Charge transfer complex, π-conjugated polymers and spin-crossover complexes are typical examples[1]. In these systems, even weak light stimulation can induce the macroscopic phase changes by virtue of

cooperative effect in the crystals. In other words, injected excess energy by photo-excitation is distributed properly into a whole crystal by cooperative physical and chemical interactions among constituent molecules to trigger the phase change from thermally stable phase to quasi-stable (thermally unstable) one. From this point of view, this exotic photo-effect is analogous to "Domino" effect as schematically shown in Figure 1 and named as photo-induced phase transition (PIPT). PIPT phenomena can be classified as a typical example of a nonequilibrium phase transition which is an important target for physics. In addition, it provides a new concept of materials design for achieving highly efficient conversion of injected photon energy. Therefore, PIPT opens an attractive field for study of basic physics, applied physics and chemistry.

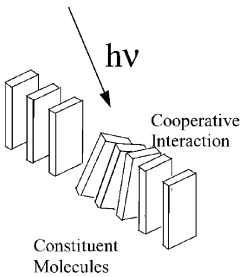

FIGURE 1 Schematics of the photo-induced 'DOMINO' effect

These previous works lead us to the idea that suitable external field cooperating with intrinsic interaction in crystals affects dynamics of PIPT. In PIPT materials, energy levels of two phases, i.e. a thermally stable one and photo-induced unstable one, are considered to be nearly degenerate due to cooperative interaction among constituents. Therefore, it is a reasonable expectation that even weak external field can affect the energy relaxation process from photo-injected localized species into the ground state (thermally stable phase) via quasi-stable one (photo-induced phase).

In this study, using spin-crossover complexes which show spin state transition between LS (S=0) and HS (S=2) by irradiating light, we demonstrate that transition speed and conversion efficiency of PIPT have been seriously affected by magnetic field. In contrast, magnetic field effect on the transition temperature (T_c) of thermal induced spin state transition was very small. The obtained results clearly indicate that magnetic field is very effective for the phase

transition dynamics under nonequilibrium condition achieved by photo-irradiation, though scarce effect was observed under thermally equilibrium condition.

CAHRACTERISTICS OF SPIN STATE PHASE TRANSITION IN SPIN-CROSSOVER COMPLEX $[Fe(2\text{-pic})_3]Cl_2EtOH$ (Fe-pic)

In spin-crossover complex $[Fe(2\text{-pic})_3]Cl_2EtOH$ (2-pic=2-amino-methyl-pyridine) (hereafter abbreviated as Fe-pic), Fe^{2+} ion and six nitrogen atoms of three 2-pic molecules take quasi-octahedral construction, and every complex is combined with three other ones via hydrogen bonds which is an origin of the cooperative interaction[2]. Figure 2 shows the crystal structure of Fe-pic observed at room temperature. There are two possible spin-configurations for spin-crossover complex, i.e. high-spin (HS) state under weak ligand field and low-spin (LS) state under rather strong one. This HS↔LS transition can be probed by magnetic and spectroscopic measurements[3]. In the case of Fe-pic, spin-crossover transition becomes spin state phase transition due to the cooperative spin-lattice interaction mediated by hydrogen bonds combining every Fe-ligand complexes. Figure 3 shows temperature dependence of the absorption spectra of Fe-pic crystals. Inset shows the temperature dependence of HS fraction estimated by magnetic measurement. Fe-pic shows the two step first order phase transition (transition temperature is 113 K and 122 K) between HS and LS states (see inset of Figure 3) [4]. As indicated in this figure, spin state phase transition in Fe-pic is accompanied with dramatic color and magnetic changes.

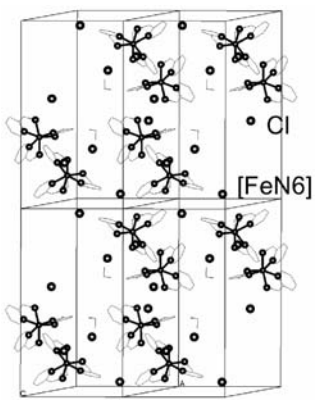

FIGURE 2 Crystal structure of Fe-pic at room temperature.

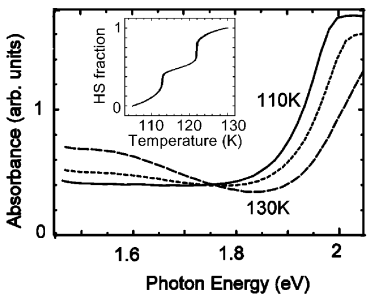

FIGURE 3 Temperature dependence of absorption spectrum of Fe-pic. Inset: Temperature dependence of HS fraction estimated by magnetic measurement.

MAGNETIC FIELD EFFECT

It is a natural expectation that the magnetic field induce an effect on the thermally driven spin state phase transition because the magnetic field stabilizes the HS state due to the difference in the magnitude of the total spin S between two phases. Under a magnetic field B, the transition temperature shift ΔT_c is expected to be given by ΔT_c=-$\Delta\chi B^2/2\Delta S$, where $\Delta\chi$ is a change of the magnetic susceptibility and ΔS is the change in entropy[5]. Indeed, this magnetic field effect has been extensively studied by various groups[5,6]. A similar magnetic field effect on T_c has been observed for Fe-pic crystal, as shown in Figure 4. Filled circles indicate transition temperatures observed in warm-up processes. When the magnetic field is increased to 7 T, transition temperature decreased by 0.2 K, which is quite small. Using the experimentally obtained values of $\Delta\chi$ and the ΔS, which have been reported previously[7], ΔT_c is estimated to be -0.18 K at B=7 T. This value is in good agreement with the experimentally observed results.

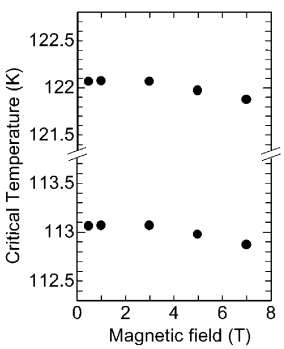

FIGURE 4 Magnetic field dependence of T_c.

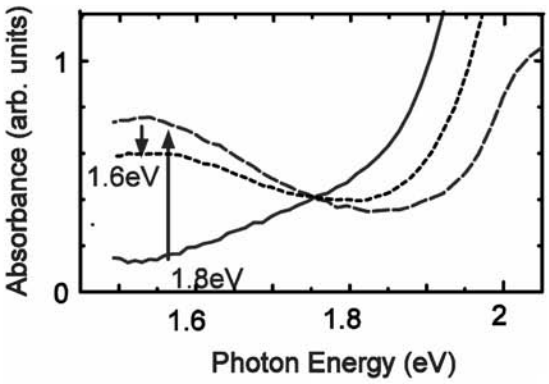

FIGURE 5 Photo-induced changes in absorption spectra in Fe-pic observed at 2 K. Solid, dashed, and dotted lines are the absorption spectra before irradiation, after 1.8eV light irradiation, and after additional irradiation by 1.6eV light, respectively.

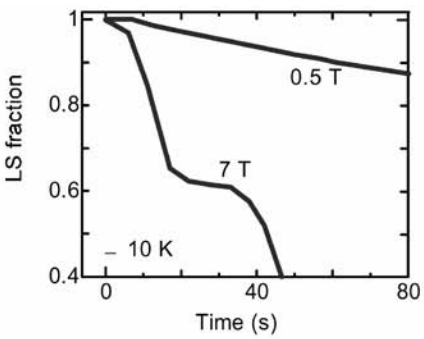

FIGURE 6 Photo-induced phase conversion dynamics from LS to HS in the magnetic field of 0.5 and 7 T at 10 K.

In Fe-pic, the spin state phase transition between the HS and LS states can be induced not only by temperature change but also by light irradiation[8,9]. At a low temperature, the crystal converts to the metastable HS state from the stable LS one by irradiating light whose photon energy is resonant to the $^1A_1 \rightarrow {}^1T_1$ absorption band (about 2.0 eV) as shown in Figure 5. The photo-converted metastable HS state is trapped in this state, and the lifetime of this state is very long because the potential barrier between the HS and LS states is sufficiently high. Furthermore it is possible that photo-transformed HS state goes back to stable LS state by irradiating the light of which photon energy is resonant to $^5T_2 \rightarrow {}^5E$ absorption band (about 1.5 eV).

In addition, in the dynamic process of photo-induced spin state conversion, the clear threshold-like behavior, the incubation period, and the occurrence of the dynamic phase separation have been observed[10]. These results demonstrate that the cooperative interaction among constituent metal-ligand complexes plays an important role in driving the photo-conversion in Fe-pic crystal, and it can be classified as a typical example of PIPT phenomena. This is the reason why we focus on the magnetic field effect on the PIPT process in Fe-pic crystal in this report.

Figure 6 shows the photo-conversion process from stable LS state to metastable HS state in magnetic fields of 0.5 and 7 T at 10 K. HS fraction was estimated by magnetic susceptibility probed by SQUID magnetometer. The photon energy of excitation light was 1.8 eV. The crystal absorbed only less than 2-3 % of the irradiation light, so the whole crystal was excited homogeneously. Increasing the magnetic filed, the conversion speed became fast in spite that the same photon-flux was utilized. The converted HS fraction observed after photo-irradiation of 50 seconds in magnetic field of 0.5, and 7 T were 0.091, and 0.65, respectively. So we can conclude that magnetic field of 7 T enhanced the photo-conversion efficiency by 7.1 times comparing with the case of 0.5 T.

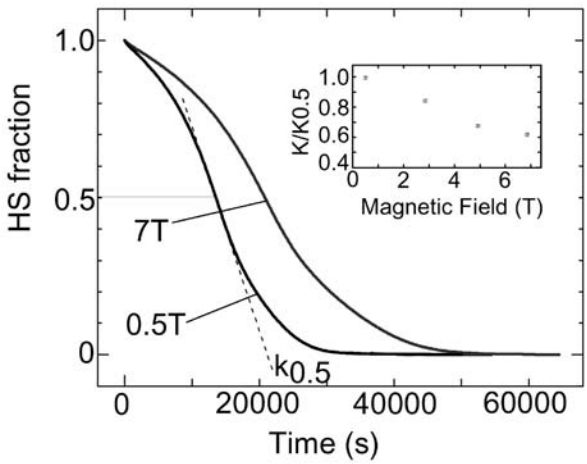

FIGURE 7 Magnetic field dependence of the relaxation process from metastable HS state to stable LS one. Metastable HS state was prepared by irradiating 2.4 eV light to the crystal in LS phase for sufficiently long interval at 10 K. Inset: An estimated relaxation rate (k) for various magnetic field observed at HS fraction was equal to 0.5. The rate was normalized by k value observed in the magnetic field of 0.5 T (denoted as $k_{0.5}$). The dashed line in the figure corresponds to the estimated k for 0.5 T (=$k_{0.5}$).

FIGURE 7 shows the magnetic field dependence of the relaxation process from metastable HS state to stable LS one. Metastable HS state was prepared by irradiating 2.4 eV light to the crystal in LS phase for sufficiently long interval. HS fraction was estimated by magnetic susceptibility probed by SQUID magnetometer at 10 K. It was observed that the metastable HS state relaxed to the stable LS state during 2-4 $\times$ 10^4 seconds and the relaxation became slow as increasing the magnetic field strength. An estimated relaxation rate (k) for various magnetic field observed at HS fraction was equal to 0.5 are plotted in the inset. The rate was normalized by k value observed in the magnetic field of 0.5 T (denoted as $k_{0.5}$). The obtained k value for 7 T was about 63 % of that observed at 0.5 T. This result clearly indicates that the magnetic field stabilizes the HS state.

CONCLUSIONS

We have reported the magnetic field effect on transition temperature, relaxation rate and conversion efficiency of the thermally and photo-induced spin state phase transition in spin crossover complex Fe-pic crystals. Obtained results clearly demonstrate that the magnetic field has a large effect on the dynamic process of PIPT. This result encourages the development of new ideas not only for the nonequilibrium dynamics of the phase transition but also for the effective control of the photochemical reaction in solid using an external magnetic field based on the cooperative interaction.

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