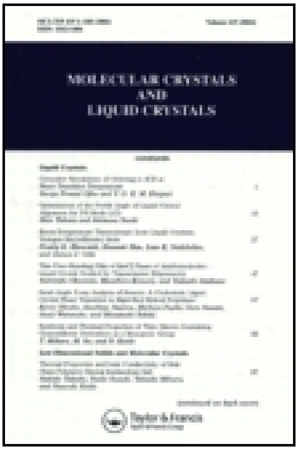

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Dynamical Aspects of the Photo-induced Spin-crossover Transition in [Fe(2-pic)$_3$]Cl$_2$·EtOH Single Crystals

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The dynamics of the photo-induced spin-crossover transition in [Fe(2-pic)$_3$]Cl$_2$·EtOH crystals has been studied by spectroscopic measurement, and we confirmed the threshold-like behavior in the excitation intensity dependence of the dynamics. The obtained results are clear evidence that the photo-induced spin-crossover transition in this crystal can be classified as photo-induced cooperative phenomena (photo-induced phase transition).

Keywords: spin-crossover; photo-induced phase transition

INTRODUCTION

Lately, extensive studies have been conducted on the photo-induced cooperative phenomena from both theoretical and experimental viewpoints. In conjugated polymers and charge-transfer (CT) crystals, it has been reported that even weak photo-excitation can trigger the macroscopic phase change by virtue of the internal electron-lattice or electron-electron interactions. In this context, this exotic phenomenon can be named as a photo-induced phase transition (PIPT). In previous works, we have made clear that the threshold-like behavior in the excitation light intensity dependence of the photo-conversion efficiency is an important characteristic of PIPT. In the followings, we demonstrate the threshold-like behavior in the excitation intensity dependence of the dynamical process of the photo-induced spin crossover transition in organometalic complex.

Here, the $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ (pic=2-aminomethylpyridine: see Fig.1(a) and (b)) has been studied as a typical example. This crystal is well known material, which shows the first-order spin-crossover transition. The Fe^{2+} atoms in this crystals take the high-spin (HS) configuration (S=2) at the temperature above the transition temperature ($T_c \cong 125K$). When the crystal is cooled down below T_c, they are converted into the low-spin (LS) configuration (S=0). Another characteristic of this transition is that the change in the spin configuration can be probed by the spectroscopic measurement.

In addition to the thermal transition, it has been reported that the photoirradiation can induce the bi-directional changes between two states at low temperature (light induced excited spin state trapping: LIESST). The possible importance of the spin-lattice cooperative interaction has been only discussed from the viewpoint of the decay kinetics of the photo-excited HS to the LS ground state[1].

The purpose of this study is to show the importance of the cooperative interaction in the dynamical process of the photo-induced change in the spin state. In other words, we demonstrate that the spin-crossover transition in this crystal can be classified as a PIPT driven by spin-lattice interaction.

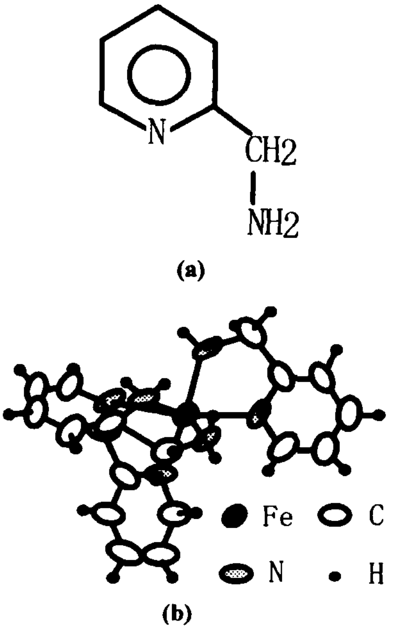

Figure 1 (a) The structure of 2-aminomethylpyridine (b) The structure of $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$[2]

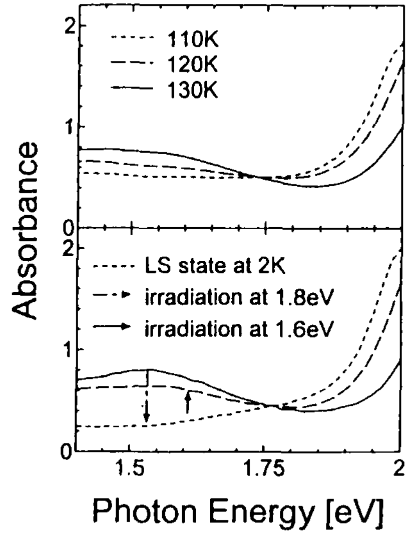

Figure 2 (a) Single-crystal absorption spectra of $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ at various temperatures. (b) Single-crystal absorption spectra of $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ before and after irradiation of 1.8eV and 1.5eV light at 2K.

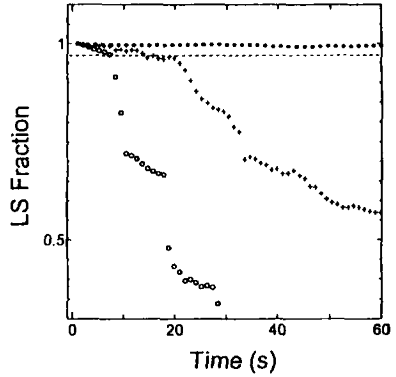

Figure 3. The molar fraction of the LS state $\gamma_{LS}(t)$ as a function of time after starting the irradiation at 2K. The photon energy of the irradiated light was 1.8eV. The excitation intensities were 4.25×10^{19} photons·cm^{-3}·s^{-1}(●), 1.13 ×10^{20} photons·cm^{-3}·s^{-1} (+), 7.00× 10^{20}photons·cm^{-3}·s^{-1} (○).

RESULT AND DISCUSSION

The samples of $[Fe(2\text{-}pic)_3]Cl_2$·EtOH were prepared by the method as described in the literature[3]. The single crystal of dimension 2.0×2.0×0.5mm^3 cleaved with razor was used for the optical measurement. $[Fe(2\text{-}pic)_3]Cl_2$·EtOH shows the two steps thermal spin transition at T_c(HS)=121K and T_c(LS)=114K. In the HS state, a very weak $^5T_2 \rightarrow ^5E$ absorption band has been observed around 1.5eV. In the LS state, two rather strong singlet-singlet transitions, $^1A_1 \rightarrow ^1T_1$ and $^1A_1 \rightarrow ^3T_1$, appear around 2.0eV and 1.3eV, respectively. Therefore the color of the crystals dramatically changes from yellow to deep red accompanied with the HS to LS transition. Fig.2(a) shows the temperature dependence of absorption spectrum of $[Fe(2\text{-}pic)_3]Cl_2$·EtOH single crystal. We estimated the fraction of the LS state by the integrated intensity of $^5T_2 \rightarrow ^5E$ and $^1A_1 \rightarrow ^1T_1$ absorption bands located at 1.5eV and 2.0eV respectively.

The LS↔HS conversion of Fe^{2+} atoms in the $[Fe(2\text{-}pic)_3]Cl_2$·EtOH crystals used here can be also induced by photo-excitation as previously reported in literature[1] (see Fig.2(b)). Irradiating the crystal in LS state with light at 1.8eV which was resonant to the $^1A_1 \rightarrow {}^1T_1$ transition, the absorption intensity around 1 and 2eV dramatically decreased and the one around 1.5eV increased. The observed spectral change can be attributed to the conversion from LS to HS state (LIESST). After the photo-conversion from LS to HS, the crystal was again irradiated with the 1.5eV light and the crystal almost went back to the original LS state as shown in this Fig.2 (b) (reverse LIESST).

To obtain the information about the dynamics of the spin state conversion, we observed the time-dependence of the converted fraction from LS to HS under the continuous light irradiation with various intensities. The results are plotted in Fig.3. The sample temperature was 2K, and thus the crystals were originally in the LS state. There are three notable points in Fig.3. The first one is an existence of the threshold intensity for starting the LS→HS transition. With the intensity weaker than 4.25×10^{19} photons$\cdot$cm$^{-3}\cdot$s^{-1} (I_{th}), crystals have shown no spectral change even after the irradiation of a few thousands of second. If the excitation light intensity became stronger than I_{th}, the occurrence of the photo-conversion from the LS to HS states was confirmed by measurement of the spectral changes. The converted fraction ($1-\gamma_{LS}$) observed after 10^3sec irradiation reached more than 80% with the intensity of 1.13×10^{20} photons$\cdot$cm$^{-3}\cdot$s^{-1}.

The second point is that a speed of the photo-conversion strongly depends on the amount of the converted fraction even though the sample was excited with the same intensities. With the excitation intensities stronger than I_{th}, the rather slow photo-conversion occurred when the converted fraction of HS state ($=1-\gamma_{LS}$) was less than 0.05±0.02 (dashed horizontal line in Fig.3). However it became larger than 0.05 ±0.02, the speed of the conversion abruptly increased (see Fig.3).

The third point is the step like increase in the converted fraction. This feature is most conspicuous with the excitation intensity of 7.00 × 10^{20}photons/cm^3·s. At the 10 and 19, 30 seconds after the starting of the irradiation, more than 10% of the LS state suddenly converted into the HS state. It is an attractive idea that the observed step-like behavior reflects the sudden generation of the domain of the HS state in the host LS crystal.

As a summary, we conformed for the first time that threshold-like behavior in the dynamics of the photo-conversion process from LS to HS state in $[Fe(2\text{-}pic)_3]Cl_2 \cdot EtOH$ single crystals. These feature clearly shows that spin-lattice cooperative interaction play a key role in photo-induced conversion between the LS and HS state. In other word, the observed exotic photo-induced phenomena can be classified as a PIPT.

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