Spectroscopic investigation of the dynamical behavior of the photoinduced phase transition of Na$_{0.6}$Co$_{1.3}$[Fe(CN)$_6$]$\cdot$4H$_2$O

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Spectroscopic investigation of the dynamical behavior of the photoinduced phase transition of Na$_{0.6}$Co$_{1.3}$[Fe(CN)$_6$]·4H$_2$O

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The dynamics of the photoinduced phase transition (PIPT) has been investigated for the Co-Fe cyanides film, Na$_{0.6}$Co$_{1.3}$[Fe(CN)$_6$]·4H$_2$O, by means of the transient absorption spectroscopy. At low temperatures (≤150 K), the compound shows the permanent PIPT from the low-spin phase [LS phase: LS Co$^{3+}$ ($t^3_2$; $t^3_3$; $e^3_1$)] to the high-spin phase [HS phase: HS Co$^{3+}$ ($t^3_2$; $t^3_3$; $e^3_1$); LS Fe$^{2+}$ ($t^3_2$; $t^3_3$)]. We have found that the film shows the transient PIPT into the HS phase above ~170 K, and the lifetime $\tau_p$ of the photoinduced phase exponentially decreased from 10 ms at 170 K to ~100 $\mu$s at 260 K. In the early stage ($\Delta t \approx 200$ ns) of the PIPT, we further have observed a characteristic photoinduced absorption band (1$\mu$m band) and ascribed the band to the LS Co$^{3+}$ ($t^3_2$; $t^3_3$; $e^3_1$) state.

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I. INTRODUCTION

The photoinduced phenomena have been extensively investigated both from the fundamental and technical points of view. In an extreme case, the photoexcitation causes the macroscopic structural change, or the so-called photoinduced phase transition (PIPT). Thus far, a long list of researchers reported the persistent PIPTs in spin-crossover complexes, transition metal cyanides, mixed-valence gold salts-type, and ascribed the band to the high-spin LS Fe$^{2+}$ ($t^3_2$; $t^3_3$; $e^3_1$) state. We have observed a characteristic photoinduced absorption band (1$\mu$m band) and ascribed the band to the LS Co$^{3+}$ ($t^3_2$; $t^3_3$; $e^3_1$) state.

Crystallographically, the Co-Fe cyanides belong to the fcc group (Fm$\overline{3}$m; Z=4), in which Co and Fe ions form a rock-salt-type (NaCl-type) network with sharing cyanido (CN$^-$) moieties. Parts of the Fe(CN)$_6$ sites, however, are vacant and are replaced by six waters (H$_2$O). Most of the Co-Fe cyanides show a first-order phase transition from the low-spin (LS) phase [LS phase: LS Co$^{3+}$ ($t^3_2$; $t^3_3$); LS Fe$^{2+}$ ($t^3_2$; $t^3_3$)] to the high-spin (HS) phase (HS phase: HS Co$^{3+}$ ($t^3_2$; $t^3_3$; $e^3_1$); LS Fe$^{2+}$ ($t^3_2$; $t^3_3$)) as temperature increases. This thermally induced phase transition accompanies a significant increase of the lattice constant $a$ from ~9.9 Å in the LS phase to ~10.3 Å in the HS phase. At low temperatures (≤150 K), a similar phase transition from the LS phase to the HS phase is induced by photoexcitation, which forcibly transfers an electron from the LS Fe$^{2+}$ to the LS Co$^{3+}$ site. Then, the photoinduced magnetism is rationally ascribed to the persistent PIPT from the (nonmagnetic) LS phase to the HS phase. The PI phase, however, melts into the LS phase as temperature increases above ~150 K.

In this paper, we have investigated the dynamical behavior of the PIPT of the Co-Fe cyanides film, Na$_{0.6}$Co$_{1.3}$[Fe(CN)$_6$]·4H$_2$O, by means of the transient absorption spectroscopy. At high temperatures, we observed a broad absorption band located at ~2.4 eV, indicating the transient PIPT into the HS phase. The lifetime $\tau_p$ of the PI phase exponentially decreases from 10 ms at 170 K to ~100 $\mu$s at 260 K. In the early stage ($\Delta t \approx 120$ ns) of the PIPT, we further have observed a characteristic photoinduced absorption band (1$\mu$m band) and ascribed the band to the LS Co$^{3+}$ ($t^3_2$; $t^3_3$; $e^3_1$) state.

For example, Sato et al. reported enhancement of magnetization in K$_{0.14}$Co[Fe(CN)$_6$]·4.93H$_2$O by irradiation of a red light (660 nm) at 5 K and suppression of magnetization by irradiation of a blue light (450 nm) at 5 K. In addition, a thin films of Co-Fe cyanide, which is indispensable for a reliable transient absorption spectroscopy, can be grown on a SnO$_2$-coated glass by the electrochemical reduction technique. Thus, we have chosen the Co-Fe cyanide as a target material for the detailed investigation on the dynamical behavior of the PIPT.
From the Fe$^{2+}$ site to the Co$^{3+}$ site. Figure 2 shows the region because of the concomitant cooperative charge transfer which significantly modifies the absorption spectrum in the visible glass according to the procedure described elsewhere.\textsuperscript{18} With Na$_{0.6}$Co$_{1.3}$\textsubscript{6}CN$_{6}$·4H$_2$O at 260 K in the LS phase (solid curve) and at 300 K in the HS phase (broken curve).

absorption band (Y band) at ≃1.7 eV, and ascribed the band to the LS Co$^{3+}$ ($t_{2g}^{3}$, $e_{g}^{1}$) state.

II. EXPERIMENTAL

A. Sample preparation and characterization

The Co-Fe cyanide film was prepared on a SnO$_2$-coated glass according to the procedure described elsewhere.\textsuperscript{18} With use of a superconducting quantum interference device (SQUID) magnetometer, we have measured temperature dependence of the magnetic susceptibility $\chi_M$ of the film. Figure 1(a) shows temperature dependence of $\chi_M T$ of the film, which is a crude measure for the effective spin moment. As seen in Fig. 1(a), the film shows the LS-to-HS transition at $T_c=306$ K in the warming run, and at $T_c=268$ K in the cooling run. Based on the thusly determined transition temperatures,\textsuperscript{22} the chemical composition of the film was estimated at Na$_{0.6}$Co$_{1.3}$\textsubscript{6}CN$_{6}$·4H$_2$O.

We show, in Fig. 1(b), absorption spectra of the Co-Fe cyanide film at 77 K in the LS phase and at 300 K in the HS phase. In both the phases, two characteristic peak structures are observed below $\sim$3.5 eV. The LS-HS phase transition significantly modifies the absorption spectrum in the visible region because of the concomitant cooperative charge transfer from the Fe$^{2+}$ site to the Co$^{3+}$ site. Figure 2 shows the magnified absorption spectra in the visible region. The spectrum indicated by broken curve stands for the photoinduced (PI) phase at 80 K, which was measured after photoexcitation by a halogen lamp for several minutes. The photoexcitation suppresses the absorption in the energy region of 2–3 eV. The spectral profile of the PI phase (broken curve) resembles with that at 300 K in the HS phase (thin solid curve\textsuperscript{17}), indicating that PI phase has the same electronic configuration as the HS phase.\textsuperscript{18}

FIG. 1. (a) Temperature dependence of $\chi_M T$ of Na$_{0.6}$Co$_{1.3}$\textsubscript{6}CN$_{6}$·4H$_2$O, where $\chi_M$ is the magnetic susceptibility. (b) Absorption spectra at 77 K in the LS phase (solid curve) and at 300 K in the HS phase (broken curve).

B. Time-resolved absorption spectroscopy

We used a nanosecond optical parametric oscillator (OPO) system pumped by a YAG laser (355 nm, 10 Hz) as an excitation source. The pulse width was 3–5 ns. For the time-resolved spectroscopy, light from a halogen lamp was focused on the sample film and the transmitted light was detected with a gatable charge-coupled device (CCD) camera attached at the output stage of a grating monochrometer. In the measurement of the small $\Delta T$ spectra, we put a polarizer in front of the monochrometer in order to eliminate the intense scattering from the excitation light. The time resolution of the system was 12 ns.

In order to obtain the overall temporal behavior of the photoinduced absorption change, we used continuous-wave lasers, e.g., He-Ne laser (1.85 eV) and yttrium aluminium garnet (YAG) laser (2.33 eV), as a probe light source. The intensity change $T_{1.85}$ eV ($T_{2.33}$ eV) of the transmitted light was detected with a P-intrinsic-N (PIN) photodiode, and the temporal behavior of $T_{1.85}$ eV ($T_{2.33}$ eV) was accumulated with a digital oscilloscope.

III. RESULTS AND DISCUSSION

A. Transient photoinduced phase transition

Figure 3(a) shows the differential absorption spectra of Na$_{0.6}$Co$_{1.3}$\textsubscript{6}CN$_{6}$·4H$_2$O at 260 K. At $\Delta t=500$ ns, the photoexcitation significantly suppresses the absorption in the energy region of 2–3 eV. The magnitude of the differential absorption decreases as the delay time $\Delta t$ increases, and eventually, the signal disappears at $\Delta t=500$ $\mu$s. The lower panel of Fig. 3 shows the differential absorption spectra of the PI phase at 80 K, which was measured after photoexcitation by a halogen lamp for several min.. The profile of the transient absorption spectra [Fig. 3(a)] resembles that of the PI phase [Fig. 3(b)]. This clearly indicates that the photoexcitation on the Fe-Co cyanide film transiently creates the HS phase.

Figure 4 shows temporal behavior of the magnitude of the transient absorption at 260 K. The vertical axis (mass fraction $\phi$) was normalized by the area of the differential absorption spectra of the PI phase. [see Fig. 3(b)] A broken curve is the best-fitted result with an exponential function, $\phi$
SPECTROSCOPIC INVESTIGATION OF THE EXCITATION SPECTRUM

The initial mass fraction $\phi_0$ of the PI phase shows a notable photon energy dependence, as shown in Fig. 5. The excitation spectrum (open circles) shows a broad maximum at 2.4 eV, and does not trace the absorption spectra of the LS phase (solid curve). This spectral difference between the excitation and absorption spectrums clearly excludes the conventional heating effect as an origin for the observed transient PITP phenomenon. The peak position of the excitation spectrum roughly coincides with first peak of an analogous system RbMn[Fe(CN)$_6$].$^{25}$ The magnitude of $\Delta$ is the same order as the transition entropy $\Delta H$ ($\approx 0.17$ eV) of an analogous system RbMn[Fe(CN)$_6$].$^{25}$ The magnitude of $\phi_0$ slightly increases with temperature. This is

![FIG. 4. Mass fraction $\phi$ of the PI phase of Na$_{0.6}$Co$_{1.3}$[Fe(CN)$_6$]·4H$_2$O at 260 K. The pulse energy and photon energy of the excitation light were 6 mJ/cm$^2$ and 2.4 eV, respectively. A broken curve is the best-fitted result with an exponential function, $\phi = \phi_0 \exp(-\Delta t/\tau)$. Open and filled circles were the data obtained at the different runs. Inset shows a single logarithm plot of $\phi$ against $\Delta t$.](Image)

![FIG. 5. Photon energy dependence of the initial mass fraction $\phi_0$ (Δt=500 ns) of the PI phase of Na$_{0.6}$Co$_{1.3}$[Fe(CN)$_6$]·4H$_2$O at 260 K. A solid curve represents the absorption spectrum of the LS phase at 77 K. The excitation energy was adjusted to 6 mJ/cm$^2$. A broken curve is merely a guide to the eyes.](Image)

![FIG. 6. Temperature dependence of (a) the lifetime $\tau_{\text{PI}}$ and (b) the initial mass fraction $\phi_0$ (extrapolation) of the PI phase of Na$_{0.6}$Co$_{1.3}$[Fe(CN)$_6$]·4H$_2$O at 260 K. The pulse energy and photon energy of the excitation light were 6 mJ/cm$^2$ and 2.4 eV, respectively. A broken curve in (a) is the best-fitted result with an exponential function.](Image)
probably because the free energy of the PI phase approaches to that of the LS ground state as temperature increases. The reduced energy difference should enhance the quantum yield of the PIPT, even though the lifetime of the PI phase shortens with temperature.

B. Initial stage of the photoinduced phase transition

Now, let us proceed to the initial stage of the transient PIPT of the Co-Fe cyanide film. Figure 7 shows the differential absorption spectra of Na0.6Co1.3[Fe(CN)6]·4H2O at 260 K. At \(\Delta t=30\) ns (the lowest spectrum), we observed a photoinduced absorption band at \(1.7\) eV, as indicated by an upward arrow. Hereafter, we will call the absorption band “Y band.” The Y band is observed only in the early state after the photoexcitation and almost disappears at \(\Delta t=200\) ns.

In order to derive the precise temporal behavior of the Y band, we decomposed the spectra into two Gauss components,

\[
\Delta \text{O.D.} = \frac{S_Y}{\sqrt{2\pi}} \exp \left[ -\frac{(\hbar \omega_Y - \hbar \omega)^2}{2\Gamma_Y^2} \right] - \frac{S_{PI}}{\sqrt{2\pi}} \exp \left[ -\frac{(\hbar \omega_{PI} - \hbar \omega)^2}{2\Gamma_{PI}^2} \right],
\]

where the spectral weight, \(S_Y\) and \(S_{PI}\), stand for the Y band and the band due to the PI phase, respectively. Overall spectral profile was adjusted by the two parameters, \(S_Y\) and \(S_{PI}\), and the other parameters are fixed as \(\hbar \omega_Y=1.75\) eV, \(\hbar \omega_{PI}=2.45\) eV, \(\Gamma_Y=0.62\) eV, and \(\Gamma_{PI}=0.77\) eV. We shows in Fig. 8 the temporal behavior of the spectral weights of the Y band (open circles) and the band due to the PI phase (filled circles). Broken curves are the best-fitted result with exponential functions. The lifetime \(\tau_Y\) of the Y band is 190 ns, which is much faster than the lifetime \(\tau_{PI}=(140\) ns) of the PI phase.

Figure 9 shows pulse energy dependence of the differential absorption spectra at 260 K. We also decomposed the spectra into two Gauss components (see Eq. (1)) and plotted the results in Fig. 10. The magnitude of \(S_Y\) linearly increases with increasing pulse energy.
as I increase in the weak excitation region (see the broken line) and then is saturated when I exceeds ~2 mJ/cm². On the other hand, the magnitude of \( S_{\text{pl}} \) is rather suppressed in the weak excitation region, but steeply increases when I exceeds ~2 mJ/cm². Such a nonlinear (or threshold) behavior is frequently observed in the permanent PIPTs.⁸,¹²-¹⁵

In order to investigate the temperature-dependent behavior, we first measured the \( \Delta T_{1.85 \text{ eV}} - \Delta T \) curve as a function of temperature. The obtained \( \Delta T_{1.85 \text{ eV}} - \Delta T \) curves were analyzed by two exponential functions

\[
\Delta T_{1.85 \text{ eV}} = A_Y \exp\left(-\frac{\Delta t}{\tau_Y}\right) - A_{\text{pl}} \exp\left(-\frac{\Delta t}{\tau_{\text{pl}}}\right),
\]

(2)

The former and the latter terms correspond to the \( Y \) band and the band due to the PI phase, respectively. The best-fitted results are shown in Fig. 11: (a) the lifetimes, \( \tau_Y \) and \( \tau_{\text{pl}} \), and (b) the amplitudes, \( A_Y \) and \( A_{\text{pl}} \). The lifetime \( \tau_Y \) [open circles in Fig. 11(a)] of the \( Y \) band show rather gradual temperature dependence, as compared to \( \tau_{\text{pl}} \) (filled circles). The activation energy \( \Delta (=0.06 \text{ eV}) \) of \( \tau_Y \) is much smaller than that \( (=0.17 \text{ eV}) \) of \( \tau_{\text{pl}} \). On the other hand, amplitude \( A_Y \) [open circles in Fig. 11(b)] of the \( Y \) band is nearly independent of temperature, being in a sharp contrast to \( A_{\text{pl}} \) (filled circles).

Now, let us discuss the origin for the \( Y \) band. The \( Y \) band has the following characteristics: (1) the lifetime \( \tau_Y \) exponentially increases as temperature decreases, (2) the signal intensity \( S_Y \) linearly increases with the excitation energy \( I \), and (3) the amplitude \( A_Y \) is independent of temperature. These characteristics suggest that the \( Y \) band is due to some self-trapped excited state. The most plausible candidate for the state is the LS \( \text{Co}^{2+} \) state \((t^3_{2g}\overline{t}^3_{2g}\overline{e}^1_{g}\overline{g})\), which is the intermediate state for the PIPT of the Co-Fe cyanide. The magnitude of \( \tau_Y \) (≈100 ns) is reasonable for such a state because the subsequent intersystem crossing into the HS \( \text{Co}^{2+} \) \((t^3_{2g}\overline{t}^3_{2g}\overline{e}^1_{g}\overline{g})\) state would take a finite time. In addition, the transition energy \( (=1.7 \text{ eV}) \) of the \( Y \) band can be explained as follows.

With the self-trapped \( \text{Co}^{2+} \) state, one may expect the additional \( t^3_{2g}\overline{t}^3_{2g}\overline{e}^1_{g}\overline{g} \rightarrow t^3_{2g}\overline{t}^3_{2g}\overline{e}^1_{g}\overline{g} \) optical transition, whose transition energy is roughly the same as the ligand-field splitting of the \([\text{Co}^{2+}(\text{NC})_6]\) complex. Then, the observed transition energy \( (=1.7 \text{ eV}) \) is reasonable, because the ligand-field splitting of the \([\text{Co}^{2+}(\text{NC})_6]\) complex should be larger than that \( (=1.04 \text{ eV}) \) (Ref. 26) of the \([\text{Co}^{2+}(\text{H}_2\text{O})_6]\) complex.

IV. SUMMARY

In summary, we have investigated the dynamical behavior of PIPT of the Co-Fe cyanide film, \( \text{Na}_6\text{Co}_{1.3}\text{[Fe(CN)]}_6\cdot4\text{H}_2\text{O} \), by means of the transient absorption spectroscopy. Based on the experimental observations, we have proposed the following process for the transient PIPT. First, the photoexcitation induces the charge transfer from the LS Fe\(^{2+}\) \((t^3_{2g}\overline{t}^3_{2g}\overline{e}^1_{g}\overline{g})\) site to the LS \( \text{Co}^{3+} \) \((t^3_{2g}\overline{t}^3_{2g}\overline{e}^1_{g}\overline{g})\) site. Immediately after the photoexcitation, the photo created LS \( \text{Co}^{2+} \) \((t^3_{2g}\overline{t}^3_{2g}\overline{e}^1_{g}\overline{g})\) state causes the \( Y \) band, whose lifetime \( \tau_Y \) is order of 100 ns. Then, the LS \( \text{Co}^{2+} \) state relaxes into the HS \( \text{Co}^{2+} \) \((t^3_{2g}\overline{t}^3_{2g}\overline{e}^1_{g}\overline{g})\) via the intersystem crossing process to cause the macroscopic HS phase.

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⁶ O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, Science 272,
The spectrum of the HT phase was for the as-grown film. The film is found to deteriorate above 320 K, which prevents us from measuring the spectrum of the thermally induced HT phase.

We have accumulated the database between the chemical composition and the transition temperatures in the Ns-Co\textsubscript{6}Fe\textsubscript{CN}\textsubscript{6}-H\textsubscript{2}O systems, which enables us to roughly estimate the chemical composition from the transition temperature.

The lifetime $\tau_{\text{Pl}}$ of the PI phase shows slight sample dependence. This is perhaps due to the different thickness and/or grain size of the film.