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Role of the intermediate state in the photoinduced process of Co-Fe cyanide

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The dynamics of the photoinduced phase transition has been investigated for the Co-Fe cyanide film, Na0.35Co[Fe(CN)6]0.79·3.7H2O, by means of the transient absorption spectroscopy. We observed two characteristic transient bands: short-lived intermediate band (I band) at ~1.9 eV and long-lived photoinduced band (PI band) at ~2.5 eV. We have found that the intensity of the I band transfers to the PI band as time exceeds, and interpreted the behavior in terms of the intersystem crossing from the photocrearted low-spin Co2+ species to the high-spin species. We further have found that the excitation spectra of these bands are qualitatively different.

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The photoinduced phenomena have been extensively investigated both from the fundamental and technical points of view. In an extreme case, the photoexcitation causes a macroscopic structural change, or the so-called photoinduced phase transition (PIPT). So far, a long list of researchers reported the permanent PIPTs in the spin-crossover complexes, the cyano-bridged metal complexes, the organic radical crystal TTTA (1,3,5-trithia-2,4,6-triazapentaleny), the polydiacetylene crystal, and so on. These materials accompany significant changes of the physical properties on the PIPT, and hence, may be utilized as opto-functional devices. In addition, there should be an important physics in the process of the PIPT. Especially, we should answer how the single photoexcitation expands into a macroscopic phase. The irreversibility of the PIPT, however, prevents the detailed investigation on the dynamics of the PIPT. Recently, Yamauchi et al. overcame the difficulty and reported a dynamics of the PIPT in the Co-Fe cyanide: their idea is that the relaxation time of the photinduced metastable state becomes faster at high temperature, which enable us to perform a time-resolved experiment.

The Co-Fe cyanides, whose chemical formula is A1Co[Fe(CN)6]y·zH2O (A = Na, K, Rb, Cs), have been attracting renewed interest of the material scientists, because they show the photoinduced magnetization as well as the photoinduced structural change. For example, Sato et al. reported enhancement of the magnetization in K0.14Co[Fe(CN)6]0.71·4.93H2O by irradiation of a red light (660 nm) at 5 K and suppression of the magnetization by irradiation of a blue light (450 nm) at 5 K. Crystallographically, the Co-Fe cyanides belong to the face-centered cubic (Fm$ar{3}$m; Z=4), in which Co and Fe ions form a rock-salt-type (NaCl-type) network bridged by the cyano (CN−) moieties. This compound has a large amount of the Fe(CN)6 vacancy, which significantly influences the magnetic and electronic properties. This is probably because the energy levels of the d-electron configuration is modified by the surrounding vacancies.

In Fig. 1, we show the electronic configurations of the neighboring Co-Fe pair. The electronic configuration at the ground state (LS phase) is Co3+ ($t^6\pi$)-Fe2+ ($t^3\pi$). The LS phase can be thermally and/or phototransferred to the PI phase with Co2+ ($t^5\pi$)-Fe2+ ($t^2\pi$). This clearly indicates that the I state, which was directly excited from the LS phase, is a Co2+ species with the intermediate state $t^5\pi$. The intermediate state $t^5\pi$ is the site density of the I state and the PI phase, respectively. $\tau_I$ and $\tau_{PI}$ are the relaxation times of the I state and PI phase, respectively. $n_I$ and $n_{PI}$ are the site densities of the I state and the PI phase, respectively.

FIG. 1. Electronic configurations of the neighboring Co-Fe pair in the low-spin phase (LS phase), photoinduced metastable phase (PI phase), and the intermediate state (I state). $\tau_I$ and $\tau_{PI}$ are the relaxation times of the I state and PI phase, respectively. $n_I$ and $n_{PI}$ are the site densities of the I state and the PI phase, respectively.

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created by the photoexcitation, play an essential role in the PIPT process. In addition, we have found that the excitation spectra are qualitatively different between the I state and the PI phase, and interpreted the phenomena in terms of the site-selective excitation.

The Co-Fe cyanide film used in this investigation was prepared on a SnO$_2$-coated glass with an electrolysis process. The details of the synthesis procedure were described elsewhere.\textsuperscript{17,18} The chemical composition was Na$_{0.35}$Co[(Fe(CN)$_6$)$_{0.79}$-3.7H$_2$O, and its thickness was \(\approx 1\) \(\mu\)m. The film shows the LS-to-HS transition at \(T_{\text{c1}} = 306\) K in the warming run, and at \(T_{\text{c1}} = 268\) K in the cooling run. All the experiments were done above \(\approx 200\) K, because the film shows the permanent PIPT below the temperature.

We first investigate the transient absorption spectra. The time-resolved spectroscopy was performed with a highly stable halogen lamp and a gatable CCD camera attached at the output stage of a grating monochrometer. The excitation light source was a second harmonics of the pulsed YAG laser (2.33 eV, 30 Hz), whose pulse width was \(3 \sim 5\) ns. This photon energy corresponds to the charge-transfer excitation from the Fe$^{2+}$ site to the Co$^{3+}$ site. Figure 2 shows a prototypical example of the differential absorption spectra of Na$_{0.35}$Co[(Fe(CN)$_6$)$_{0.79}$-3.7H$_2$O at 260 K. Soon after the photoexcitation, we observed two characteristic transient bands at \(\approx 1.9\) eV (denoted as the I band) and at \(\approx 2.5\) eV (PI band). The overall spectral profiles are consistent with Ref. 16. The latter band can be ascribed to the transient PI phase,\textsuperscript{16} because its spectral profile resembles that of the permanent PI phase measured at 90 K (not shown). Assuming \(n_{\text{PI}} = 1\) after the permanent PIPT at 90 K,\textsuperscript{19} the site density \(n_{\text{PI}}\) of the PI phase at 260 K and at \(t = 100\) ns is estimated to be \(0.17\). Accordingly, the quantum efficiency of the PI phase is estimated to be \(\approx 5\) sites/photon. On the other hand, the former band is ascribed to the LS Co$^{2+}$ species (I state in Fig. 1),\textsuperscript{16} judging from the much shorter lifetime \(\tau_I\) (\textit{vide infra}). Both the absorption bands completely disappear at 10 ms.

Now, let us proceed to the temporal evolution of the respective bands. The temporal behavior of the I band (PI band) was monitored with a continuous wave He-Ne laser at 1.96 eV (YAG laser at 2.33 eV) and a digital oscilloscope (Textronics TDS5104B). In Fig. 3, we summarized the temperature dependence of the lifetimes, \(\tau_I\) and \(\tau_{\text{PI}}\), for the respective bands. These lifetimes were almost constant irrespective of the pulse energy \(I_{\text{pump}}\) (1 mJ/cm$^2 \approx I_{\text{pump}} \leq 7$ mJ/cm$^2$). The magnitude of \(\tau_{\text{PI}}\) increases as the temperature decreases. As shown in the inset, \(\tau_{\text{PI}}\) nearly obeys the Arrhenius relation with the activation energy \(E_{\text{a}} = 0.22\) eV. Kawamoto \textit{et al.}\textsuperscript{20} performed an \textit{ab initio} cluster calculation on the Co(NC)$_5$·H$_2$O cluster, and derived the total energy as a function of the Co-N bond distance. Based on their calculation, the potential barrier between the LS Co$^{3+}$ state and the HS Co$^{2+}$ state is \(\approx 0.5\) eV. The calculated value is in good agreement with the experiment, taking account of the tendency that the cluster calculation usually overestimates the energy difference. On the other hand, the magnitude of \(\tau_I\) is much shorter than \(\tau_{\text{PI}}\), and is nearly constant (\(\approx 300\) ns) irrespective of temperature.

Figure 4 shows the temporal evolution of \(n_{\text{PI}}\) at 215, 230, and 250 K, monitored by the transmitting change at 2.33 eV. The fast component (\(\leq 20\) ns) seen in Fig. 4 is due to the stray of the excitation light. \(n_{\text{PI}}\) shows a characteristic behavior; at 215 K, for example, \(n_{\text{PI}}\) gradually increases to \(\approx 0.09\) within \(\approx 1\) \(\mu\)s, and then gradually decreases beyond 10 \(\mu\)s. Such a flow-in (flow-out) behavior of the \(n_{\text{PI}}\) curve strongly suggests that the PI phase is not directly created by the photoexcitation, but is gradually converted from the photoinduced I state (see Fig. 1). In order to confirm this scenario, we analyzed the \(n_{\text{PI}}\) curve by a rate equation including the three energy levels, i.e., the LS phase, the I state, and the PI phase. The temporal evolution of \(n_{\text{PI}}(t)\) is expressed as

\[
\begin{align*}
\frac{dn_{\text{PI}}}{dt} &= k_{\text{in}} n_I - (k_{\text{out}} + k_{\text{decomp}}) n_{\text{PI}} \\
&= k_{\text{in}} n_I - k_{\text{out}} n_{\text{PI}}
\end{align*}
\]

FIG. 2. Differential absorption spectra of Na$_{0.35}$Co[Fe(CN)$_6$]$_{0.79}$-3.7H$_2$O at 260 K. The pulse energy and the photon energy of the excitation light were 5 mJ/cm$^2$ and 2.33 eV, respectively. Thick and thin curves are measured at 100 ns and 10 ms. We call the \(\approx 1.9\) eV band and the \(\approx 2.5\) eV band as the I band and the PI band, respectively.

FIG. 3. Temperature dependence of the lifetimes for the PI band (\(\tau_{\text{PI}}\): open circles) and for the I state (\(\tau_I\): closed circles). The pulse energy and the photon energy of the excitation light were 7 mJ/cm$^2$ and 2.33 eV, respectively. The inset shows the Arrhenius plot of \(\tau_{\text{PI}}\).
FIG. 4. Temporal evolution of the site density $n_{\text{PI}}$ of the PI phase of the Na$_{0.35}$Co[Fe(CN)$_6$_{$0.79$}·3.7H$_2$O film at 215, 230, and 250 K. The pulse energy and the photon energy of the excitation light were 5 mJ/cm$^2$ and 2.33 eV, respectively. The gray curves are the fitted results of the three-level model (see text).

\[ n_{\text{PI}}(t) = \frac{\tau_{\text{PI}}}{\tau_{\text{I}} - \tau_{\text{I}}} n_0^I (e^{-t/\tau_{\text{I}}} - e^{-t/\tau_{\text{PI}}}) , \]

where $n_0^I$ is the initial site density of the I state after the photoexcitation. Here, we emphasize that only the magnitude $\frac{\tau_{\text{I}}}{\tau_{\text{PI}}}$ is the fitting parameter of Eq. (1), because we already know the temperature dependence of the lifetimes, i.e., $\tau_{\text{I}}$ and $\tau_{\text{PI}}$ (see Fig. 3). This simple model well reproduces the experimentally obtained $n_{\text{PI}}$ vs. $t$ curves, as shown by the gray curves in Fig. 4.

Based on these analyses, we propose a possible PIPT process of the Co-Fe cyanide. First, the charge-transfer excitation creates the LS Co$^{2+}$-LS Fe$^{3+}$ pair within $\sim$150 fs, forming the so-called Frank-Condon state. This Frank-Condon state elongates the Co-Fe bond distance, because the ionic radius $r_{\text{LSCo}}^{2+}$ (≈0.65 Å)$^{22}$ of the LS Co$^{2+}$ ion is larger than $r_{\text{LSCo}}^{3+}$ (≈0.545 Å) of the LS Co$^{3+}$ ion. Actually, the lattice constant $a$ increases from $\approx$9.9 Å in the LS phase (Co$^{3+}$-Fe$^{2+}$ configuration) to $\approx$10.3 Å in the thermally induced charge-transfered phase (Co$^{2+}$-Fe$^{3+}$ configuration).$^{10}$

The lattice relaxation is considered to spread around the charge-transfered pair to reduce the strain energy. In our preliminary ultrafast experiment,$^{21}$ we found that the conversion efficiency is fairly reduced if we shorten the excitation light pulse from 2 to 3 ns to 100 fs at the same photon energy ($\approx$0.3 eV) and photon number ($\approx$1.3 $\times$ 10$^{16}$/cm$^2$/pulse). This observation implies that some state is formed within a few ns, which enhances the conversion efficiency. We think that the state is a cluster state of the charge-transfered pairs. As time exceeds $\sim$300 ns, the LS Co$^{2+}$ species change into the HS ones via the intersystem crossing. As a result, the metastable PI phase with the HS

FIG. 5. (a) Excitation photon energy dependence of the site density $n_{\text{PI}}$ of the PI phase of Na$_{0.35}$Co[Fe(CN)$_6$_{$0.79$}·3.7H$_2$O at 260 K (cited from Ref. 16). (b) Excitation photon energy dependence of the site density $n_{\text{I}}$ of the I phase, monitored by the transmission change at 1.96 eV. (c) Absorption spectra at 77 K in the LS phase. Broken curves in (a) and (b) are merely the guide to the eyes.

Co$^{2+}$-LS Fe$^{3+}$ configuration is formed. We believe that the interaction between the charge-transfered pairs mediated by the lattice relaxation is essential for the formation of the transient PI phase, which means the charge-transfered cluster with cooperative lattice distortion. First, the quantum efficiency of the PI phase ($\sim$5 sites/photon) is much larger than unity, suggesting an energy transfer mechanism of the excess energy to the unexcited pairs. Second, the activation energy $E_\infty$ ($\approx$0.22 eV) of $\tau_{\text{PI}}$ is consistent with the cluster calculation,$^{20}$ suggesting that the lattice relaxation is important for the formation of the PI phase.

Finally, let us discuss the excitation spectra for the PI band and the I state (see Fig. 5). To obtain the excitation spectrum, the energy of the excitation light source (3.49 eV, 30 Hz) was converted with a nanosecond optical parametric oscillator (OPO) system. The excitation spectrum for the PI band [Fig. 5(a)] shows a single peak at $\sim$2.4 eV, which seems to be enhanced around the first peak ($\sim$2.1 eV) of the absorption $\alpha(\omega)$ spectrum of the LS phase [Fig. 5(c)]. This spectral difference between the excitation spectrum and the $\alpha(\omega)$ spectrum clearly excludes the conventional heating effect as an origin for the observed transient PIPT phenomenon. On the other hand, the excitation spectrum for the I state [Fig. 5(b)] rather traces the $\alpha(\omega)$ spectrum. In other words, the quantum efficiency increases at both the first ($\sim$2.1 eV) and the second ($\sim$3.2 eV) peak of the $\alpha(\omega)$ spectrum. These excitation spectra indicate that the formation of the I state is not the sufficient condition for the PIPT into the PI phase.

To deepen the argument, we first have to assign the first and second absorption peaks. The first peak, or the absorp-
tion edge, was assigned to the charge-transfer (CT) excitation from the Fe$^{3+}$ site to the Co$^{3+}$ site, while the origin for the second peak remains unclear. Kawamoto et al. have performed an \textit{ab initio} calculation on the Co(CN)$_3$·H$_2$O cluster and the Co(CN)$_6$ cluster, and found that the resonant energy of the CT excitation significantly increases from −2.3 eV for former cluster to −3.9 eV for the latter cluster. They also found that the energy difference between the ground state (the LS phase) and the PI phase also increases from −0 eV for the former cluster to 1.5 eV for the latter cluster. Therefore, we assigned the first (second) absorption peak to the CT excitation on the Co(CN)$_3$·H$_2$O cluster [the Co(CN)$_6$ cluster]. In an actual compound, however, there exists the spatial inhomogeneity of the vacancies, which causes the vacancy-rich and vacancy-poor regions.

Based on the above-mentioned assignment, the observed excitation spectra (Fig. 5) are interpreted as follows. The photoexcitation of the first peak selectively induces the charge-transfer in the vacancy-rich regions. In this region, $\tau_{PI}$ is considered to be much longer than $\tau_1$ (=300 ns), because the energy difference between the LS phase and the PI phase is negligible. Then, the PI state should accumulate in the flow-in (flow-out) process (see Fig. 1). On the other hand, the excitation of the second peak excitation induces the charge-transfer in the vacancy-poor regions. In this region, $\tau_{PI}$ is comparable with $\tau_1$ (=300 ns), since the energy difference is much larger. In this case, the fast relaxation of the PI state prevents the accumulation of the state. An analogous situation can be realized if we reduce the magnitude of $\tau_{PI}$ (see Fig. 4). One may notice that the magnitude of $n_{PI}$ is suppressed as temperature increases; $\tau_{PI}$ decreases from $=0.09$ at 215 K ($\tau_{PI}=20 \mu$s) to $=0.05$ at 250 K ($\tau_{PI}=8 \mu$s).

In summary, we have investigated the dynamical behavior of PIPT of the Co-Fe cyanide, Na$_{0.35}$Co[Fe(CN)$_6$]·0.79·3.7H$_2$O, by means of the transient absorption spectroscopy. We observed a clear flow-in (flow-out) behavior of $n_{PI}$, which is quantitatively reproduced by the rate equation including three energy levels, i.e., the LS phase, the I state and the PI phase. Our observations suggest that the I state, whose lifetime is $\sim$300 ns, plays an essential role in the PIPT process of the Co-Fe cyanide. We believe this is a first step to clarify how the single photoexcitation expands into a macroscopic phase.

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19 We investigated the differential absorption spectrum as a function of photoirradiation time at 90 K. The spectral change was almost saturated in 30 s.
21 Kamioka et al. (unpublished).
23 The probability to find the Co(CN)$_6$·H$_2$O cluster [the Co(CN)$_6$ cluster] is 0.32 (0.14), if we assume the random distribution of the [Fe(CN)$_6$]$_2$ vacancies.