

# Dynamics of charge-transfer pairs in the cyano-bridged $\text{Co}^{2+}\text{-Fe}^{3+}$ transition-metal compound

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Dynamics of the charge-transfer (CT) pairs has been investigated for the cyano-bridged  $\text{Co}^{2+}\text{-Fe}^{3+}$  particles grown in a hydrophilic cavities of Nafion 117 film. We decomposed the differential absorption spectra into the fast and slow components. We ascribed the fast and slow components to the Frank-Condon state and the CT ( $\text{Co}^{3+}\text{-Fe}^{2+}$ ) pairs with lattice relaxation, respectively. We found that the lifetime  $\tau_{\text{CT}}$  of the pairs at 10 K increases with the absorbed photon density  $n$  from  $\tau_{\text{CT}} \approx 2$  ns to  $\approx 6$  ns, reflecting the attractive interaction between the pairs.

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The photoinduced phenomena<sup>1</sup> 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,<sup>2-5</sup> the cyano-bridged metal compound,<sup>6-12</sup> the mixed-valence gold complex,  $\text{Cs}_2\text{Au}_2\text{Br}_6$ ,<sup>13</sup> the iodine-bridged binuclear Pt compounds,<sup>14</sup> the organic radical crystal, 1,3,5-trithia-2,4,6-triazapentalenyl,<sup>15</sup> the polydiacetylene crystal,<sup>16</sup> and so on. A significant feature of the photoinduced effect is that we can expect a transient *hidden phase* that can be created only by the photoexcitation. For example, Moritomo *et al.*<sup>17</sup> performed the nanosecond time-resolved experiment for the film of a cyano-bridged metal complex,  $\text{Na}_{0.35}\text{Co}[\text{Fe}(\text{CN})_6]_{0.79} \cdot 3.7\text{H}_2\text{O}$ , and found a two-step relaxation behavior. The photoexcitation transfers an electron from the low-spin  $\text{Fe}^{2+}$  to the low-spin  $\text{Co}^{3+}$ , and causes the unconventional CT pairs, low-spin  $\text{Co}^{2+}\text{-Fe}^{3+}$ . These unconventional pairs form a transient hidden phase,<sup>18</sup> whose lifetime is pretty long ( $\approx 300$  ns). Eventually, the phase relaxes to the metastable phase, high-spin  $\text{Co}^{2+}\text{-Fe}^{2+}$ , via the inter-system crossing of  $\text{Co}^{2+}$ .

Among the photosensitive materials, the Prussian Blue-type cyano-bridged Co-Fe compound, whose formula is  $A_x\text{Co}[\text{Fe}(\text{CN})_6]_y \cdot z\text{H}_2\text{O}$  ( $A=\text{Na, K, Rb, Cs}$ ), is attracting renewed interest of the material scientists, because they show the photoinduced magnetization<sup>6,7</sup> as well as the photoinduced structural change.<sup>10</sup> The compound consists of the a rock-salt-type (NaCl-type) cyano-bridged metal network,  $-\text{CN-Co-NC-Fe-CN-Co-}$ . Characteristic feature of the compound is the thermally induced charge-transfer transition from the low-temperature phase,  $\text{Fe}^{2+}(t_{2g}^6)\text{-Co}^{3+}(t_{2g}^6)$ , to the high-temperature phase,  $\text{Fe}^{3+}(t_{2g}^5)\text{-Co}^{2+}(t_{2g}^5e_g^2)$ .<sup>11</sup> The photoexcitation at 5 K (Refs. 6 and 7) also induces the charge-transfer transition from the nonmagnetic low-temperature phase to the ferrimagnetic high-temperature phase, causing the photoinduced magnetization.

In this Rapid Communication, we have investigated the dynamics of the CT pairs in the cyano-bridged Co-Fe compound,  $\text{Co}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_{2/3}5\text{H}_2\text{O}$ . The compound does not contain the alkaline metal ions, and takes the electronic configuration of the high-temperature phase, that is,  $\text{Fe}^{3+}$

( $t_{2g}^5$ )- $\text{Co}^{2+}$  ( $t_{2g}^5e_g^2$ ), down to the lowest temperature. The compound becomes ferrimagnetic below 14 K in the bulk form.<sup>19</sup> We decomposed the differential absorption spectra into the fast and slow components, and ascribed the components to the Frank-Condon state and the CT ( $\text{Co}^{3+}\text{-Fe}^{2+}$ ) pairs with lattice relaxation, respectively. We found that the lifetime  $\tau_{\text{CT}}$  of the pairs at 10 K increases with the absorbed photon density  $n$  from  $\tau_{\text{CT}} \approx 2$  ns to  $\approx 6$  ns, reflecting the attractive interaction between the pairs.

The cyano-bridged  $\text{Co}^{2+}\text{-Fe}^{3+}$  particles were grown in the hydrophilic cavities of Nafion 117 film.<sup>20</sup> The Nafion film, whose thickness is 180  $\mu\text{m}$ , was immersed in an aqueous solution of  $\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$  ( $0.5 \text{ mol dm}^{-3}$ ) for 1 h. After drying under air, it was placed in an aqueous solution of  $\text{Co}^{\text{II}}\text{Cl}_2$  ( $0.1 \text{ mol dm}^{-3}$ ) for 1 h, to form Prussian Blue analogs inside the cavities. To remove excessive Co ions, the film was dipped in an aqueous solution of KCl ( $1 \text{ mol dm}^{-3}$ ) for 20 minutes, rinsed with distilled water, and dried under air. The color of the film was transparent brown and is suitable for the time-resolved spectroscopy. An inductively coupled plasma mass spectroscopy showed that the ratio of the Co and Fe in the particle was 0.67, indicating the formula of the particle was  $\text{Co}[\text{Fe}(\text{CN})_6]_{2/3}5\text{H}_2\text{O}$ . A synchrotron-radiation x-ray powder diffraction measurement at SPring-8 BL02B2 beamline revealed that the lattice structure is cubic ( $Fm\bar{3}m; Z=4$ ). The lattice constant  $a$  is 1.02941(4) nm, which is comparable with the bulk  $\text{Co}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_{2/3}5\text{H}_2\text{O}$  [ $a=1.032$  nm (Ref. 7)]. With use of Scherrer's equation, the mean particle size was estimated to be  $\sim 9.3 \pm 1.5$  nm.

The ultrafast time-resolved spectroscopy was carried out in a pump-probe configuration at room temperature and 10 K. We employed a regenerative amplified Ti:sapphire laser with a pulse width of 100 fs and repetition rate of 1000 Hz as the light source. The pump pulse energies were 1.55 and 3.10 eV, the latter was generated as second harmonics in a  $\beta\text{-BaB}_2\text{O}_4$  crystal. The frequency of the pump light was decreased by half (500 Hz) to provide "pump-on" and "pump-off" conditions. The white probe pulse, generated by self-phase modulation in a sapphire plate, was focused on the sample with the pump pulse. The transmitted probe spectrum was detected by a 72ch Si-photodiode array attached to a 30 cm imaging spectrometer. The temporal profiles of all

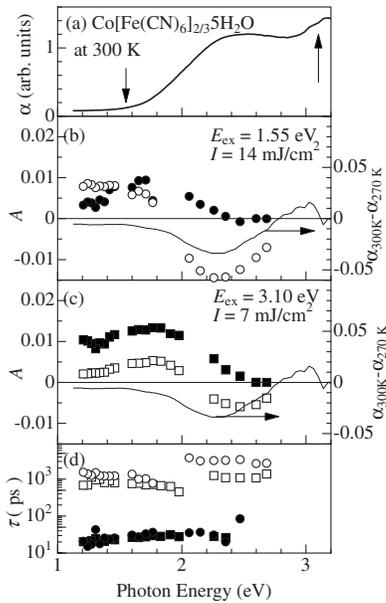


FIG. 1. (a) Absorption spectra of  $\text{Co}[\text{Fe}(\text{CN})_6]_{2/3}\cdot 5\text{H}_2\text{O}$  particles embedded in the Nafion 117 film at 300 K. Upward and downward arrows represent the excitation photon energy  $E_{\text{ex}}$ . (b) Magnitudes  $A$  of the fast (filled circles) and slow (open circles) components at  $E_{\text{ex}}=1.55$  eV. (c) Magnitudes  $A$  of the fast (filled squares) and slow (open squares) components at  $E_{\text{ex}}=3.10$  eV. (d) Lifetimes for the fast (filled circles and squares) and slow (open circles and squares) components. The circle and square symbols mean that the data points are obtained at  $E_{\text{ex}}=1.55$  eV and 3.10 eV, respectively. Thin curves shown in (b) and (c) are the thermally differential absorption spectra,  $\alpha_{300\text{K}}-\alpha_{270\text{K}}$ , of the same film, where  $\alpha_{300\text{K}}$  ( $\alpha_{270\text{K}}$ ) represent the absorption spectra measured at 300 K (270 K).

channels were recorded at once through a multichannel analog-digital converter. The differential absorption spectra were calculated by subtraction of the successive probe pulse intensities, were accumulated for 3000–10000 pulses, and were recorded as a function of probe delay time. This system enables us to observe the absorption change between 1.2 eV and 2.7 eV. We first confirmed that the Nafion 117 film without cyano particles shows negligible photinduced signal ( $\leq 0.002$ ) even at the highest excitation power.

The top panel of Fig. 1 shows the absorption spectra of  $\text{Co}[\text{Fe}(\text{CN})_6]_{2/3}\cdot 5\text{H}_2\text{O}$  particles at 300 K. The spectrum consists of a lower-lying band at 2.4 eV and a higher-lying band at 3.0 eV. The lower-lying band is ascribed to the transfer of an electron from  $\text{Co}^{2+}$  to  $\text{Fe}^{3+}$  (CT band), while the higher-lying one is to that from the ligand ( $\text{CN}^-$ ) to  $\text{Fe}^{3+}$  within the  $[\text{Fe}(\text{CN})_6]$  complex (LMCT band).<sup>11</sup> The 1.55 eV photon [downward arrow in Fig. 1(a)] excited the tail region of the CT band, while the 3.10 eV photon (upward arrow) resonantly excites the LMCT band. Thus, the excitation photon energy dependence on the charge-transfer dynamics will give us clues to interpret the differential absorption spectra.

Figure 2 shows prototypical decay curves for  $\text{Co}[\text{Fe}(\text{CN})_6]_{2/3}\cdot 5\text{H}_2\text{O}$  particles at the respective probe photon energies at 300 K: (a) the CT excitation condition and (b) the LMCT excitation condition. At both the conditions, absorption saturation ( $\Delta\text{O.D.} \leq 0$ ) is observed in the high en-

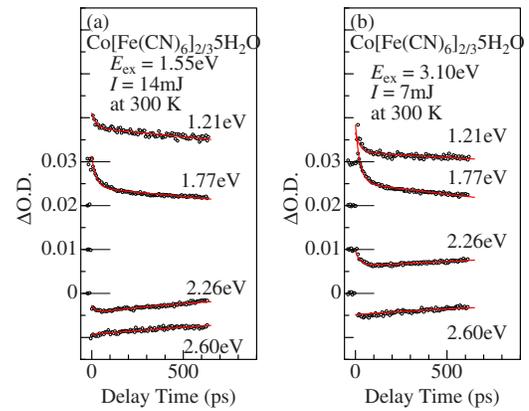


FIG. 2. (Color online) Prototypical decay curves of  $\text{Co}[\text{Fe}(\text{CN})_6]_{2/3}\cdot 5\text{H}_2\text{O}$  particles at the respective probe photon energies at 300 K at (a)  $E_{\text{ex}}$  (excitation photon energy) = 1.55 eV and (b)  $E_{\text{ex}}=3.10$  eV. The respective decay curve is shifted by +0.01. Solid curves are the results of the least-squares fitting with two exponential functions:  $\Delta\text{O.D.} = A_{\text{fast}} \exp(-t/\tau_{\text{fast}}) + A_{\text{slow}} \exp(-t/\tau_{\text{slow}})$ .

ergy region above 2.26 eV, while induced absorption ( $\Delta\text{O.D.} \geq 0$ ) is observed in the low energy region below 1.77 eV. These decay curves show the two component behavior, which is most remarkable in the 1.77 eV curve. We analyzed the curves with two exponential functions:  $\Delta\text{O.D.} = A_{\text{fast}} \exp(-t/\tau_{\text{fast}}) + A_{\text{slow}} \exp(-t/\tau_{\text{slow}})$ . As seen in Fig. 2, the exponential function satisfactorily reproduces the experimental data, as indicated by the solid curves in Fig. 2.<sup>21</sup> We emphasize that no long-lived constant term is needed to reproduce the data, indicating that the sample heating effect is negligible.

Thus obtained magnitudes,  $A_{\text{fast}}$  and  $A_{\text{slow}}$ , and lifetimes,  $\tau_{\text{fast}}$  and  $\tau_{\text{slow}}$ , for the respective components are plotted in Figs. 1(b)–1(d). The circle and square symbols mean that the data points are obtained at the CT and LMCT excitation conditions, respectively. The filled and open symbols represent the fast and slow components, respectively. Here, we emphasize that both the fast and slow spectra shown in Figs. 1(b) and 1(c) are qualitatively different from the thermally differential spectra (thin curves). Especially, the thermally differential spectrum shows no positive component below  $\sim 2$  eV. This clearly indicates that even the slow component spectra cannot be ascribed to the conventional thermal effect.

In both the excitation conditions [see Figs. 1(b) and 1(c)], considerable spectral weight was observed in the fast component (filled circles). The lifetime  $\tau_{\text{fast}}$  scatters in the range from 20 to 30 ps. We tentatively ascribe the component to the Frank-Condon state or the charge-transfer state without local lattice relaxation. In the CT excitation condition, the fast spectrum is dominated by the  $\text{Co}^{3+}\text{-Fe}^{2+}$  state. The state triggers the local lattice distortion, or the reduction of the Co-Fe bond distance, to form the self-trapped CT pair. The formation time of such a self-trapped state is 25 ps. In the LMCT excitation condition, the spectrum is dominated by the  $\text{CN-Fe}^{2+}$  state. The state relax to the ground state or to the self-trapped CT pair via the successive electron transfer from  $\text{Co}^{2+}$  to the neutral CN.

The slow component (open circles), on the other hand, is significantly enhanced in the CT excitation condition [see

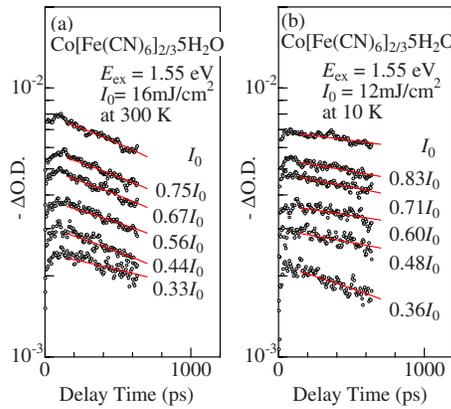


FIG. 3. (Color online) Excitation energy dependence of relaxation curves at 2.4 eV for  $\text{Co}[\text{Fe}(\text{CN})_6]_{2/3}\cdot 5\text{H}_2\text{O}$  particles at (a) 300 K and (b) 10 K. Solid curves are the results of the least-squares fitting (see text).

Fig. 1(b)], suggesting that the component is due to the self-trapped CT pairs. Then, the higher-lying absorption saturation is ascribed to reduction of the number of the original CT ( $\text{Co}^{2+}\text{-Fe}^{3+}$ ) pairs that is responsible for the CT band. The lower-lying photoinduced absorption can be ascribed to the  $\text{Co}^{3+}$  state with unconventional spin state, that is, the high-spin ( $t_{2g}^4 e_g^2$ ) state and the intermediate-spin ( $t_{2g}^5 e_g^1$ ) states. First, there is no absorption band in the low-temperature phase of the Co-Fe cyanide with low-spin  $\text{Co}^{3+}$ .<sup>11</sup> Second, the photoinduced charge transfer from the high-spin  $\text{Co}^{2+}$  ( $t_{2g}^5 e_g^2$ ) to  $\text{Fe}^{3+}$  site creates the high-spin  $\text{Co}^{3+}$  or the intermediate-spin  $\text{Co}^{3+}$ , but directly cannot create the low-spin  $\text{Co}^{3+}$  ( $t_{2g}^6$ ). With such unconventional  $\text{Co}^{3+}$  ions, extra absorptions are expected below 2 eV due to the intra-atomic  $d\text{-}d$  transition.<sup>22</sup> Looking at Fig. 1(c), one may notice that some part of the LMCT excitation creates the CT pairs. The quantum yield  $\eta_{\text{LMCT}}$  [number of the CT pair created by one absorbed photon] in the LMCT excitation condition, however, is very small [ $=0.20\eta_{\text{CT}}$ :  $\eta_{\text{CT}}$  is the quantum yield in the CT excitation condition], since the extra electron transfer from  $\text{Co}^{2+}$  to the neutral CN is needed.

We investigated the lifetime  $\tau_{\text{CT}}$  of the CT pairs as a function of the excitation energy  $I$  in the CT excitation condition. Figure 3 shows decay curves of the CT pair for  $\text{Co}[\text{Fe}(\text{CN})_6]_{2/3}\cdot 5\text{H}_2\text{O}$  particles. The lifetime  $\tau_{\text{CT}}$  corresponds to the inverse number of the slope (see straight lines in Fig. 3). The increase of the data points in the early stage ( $\leq 50$  ps) is due to the overlap of the fast component. At 10 K [Fig. 3(b)], the magnitude of  $\tau_{\text{CT}}$  significantly increases as  $I$  increase. We have estimated the magnitude  $A_{\text{CT}}$  and the lifetime  $\tau_{\text{CT}}$  for the CT pairs, and plotted them in Fig. 4 against the absorbed photon density  $n$ . At 300 K (filled circles),  $\tau_{\text{CT}}$  is nearly independent of  $n$  and  $A_{\text{CT}}$  linearly increases with  $n$ . At 10 K (open circles), magnitude of  $\tau_{\text{CT}}$  increases with  $n$  from  $\approx 2$  ns at  $n=0.002$  photon/Co to  $\approx 6$  ns at 0.006 photon/Co even though no nonlinear behavior is observed in  $A_{\text{CT}}$ . The lifetime elongation behavior was observed only in the CT excitation condition, in which the photon energy is efficiently used to create the CT pairs.

The observed lifetime elongation is considered to be as-

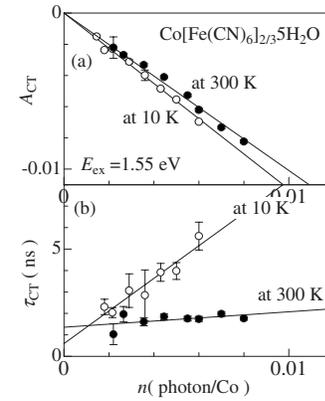


FIG. 4. (a) Magnitude  $A_{\text{CT}}$  and (b) lifetime  $\tau_{\text{CT}}$  of the CT pair as a function of absorbed photon density  $n$  for  $\text{Co}[\text{Fe}(\text{CN})_6]_{2/3}\cdot 5\text{H}_2\text{O}$  particles at 10 K (open circles) and 300 K (filled circles). Solid lines are merely guides to the eyes.

cribed to the attractive interaction between the photocreated CT pairs, which is mediated by the local lattice distortion, the electrostatic potential, and so on. In a weak excitation condition, the CT pairs are separated from each other. Then, the  $\tau_{\text{CT}}$  ( $\approx 2$  ns) is considered to be the intrinsic lifetime of a single pair. In a stronger excitation condition, however, the CT pairs merge to form a cluster state. In such a cluster state, the attractive interaction further stabilizes the pair to cause the lifetime elongation as observed. The absorbed photon density  $n$  ( $\leq 0.01$ ),<sup>23</sup> however, is still low in the CT excitation condition. Then, we expect a more significant lifetime elongation in the resonant CT excitation condition. A similar lifetime elongation is reported in a ferromagnetic doped manganite. Liu *et al.*<sup>24</sup> have investigated the lifetime of the photoinduced spin disordered state for  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  film grown on the  $\text{SrTiO}_3$  (001) substrate, whose Curie temperature  $T_C$  is 262 K. They observed that the lifetime  $\tau$  at 235 K ( $\leq T_C$ ) increases from 68 ns at  $I=1.2$  mJ/cm<sup>2</sup> to 1262 ns at  $I=6.7$  mJ/cm<sup>2</sup> even though the signal intensity  $A$  linearly increases with  $I$ . In addition, the  $\tau$  value critically increases on approaching  $T_C$  as  $\tau \propto (|T/T_C - 1|)^{-1.39}$ . The critical behavior as well as the lifetime elongation were ascribed to the formation of the charge-ordering clusters,<sup>25</sup> which intrinsically exist above  $T_C$ .

In summary, we have investigated the dynamics after the charge-transfer excitation for  $\text{Co}[\text{Fe}(\text{CN})_6]_{2/3}\cdot 5\text{H}_2\text{O}$  particles embedded in the Nafion 117 film. We decomposed the differential absorption spectra into the fast and slow components, and ascribed them to the Frank-Condon state and the CT pair ( $\text{Co}^{3+}\text{-Fe}^{2+}$ ) with lattice relaxation. The formation time of the CT pair is 25 ps. We observed a lifetime elongation of the pairs at 10 K, which is a precursor of the formation of a transient *hidden phase* with unconventional spin state of  $\text{Co}^{3+}$  ions.

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