Electronic phase diagram of valence-controlled cyanide: Na$_{0.84}$Co$_{0.71}$[Fe(CN)$_6$]$_{3.8}$H$_2$O (0 $\leq$ $\delta$ $\leq$ 0.61)

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Electronic phase diagram of valence-controlled cyanide: \( \text{Na}_{0.84-\delta}\text{Co}[\text{Fe(CN)}_6]_{0.71-0.61} \cdot 3.8\text{H}_2\text{O} \) 

\((0 \leq \delta \leq 0.61)\)

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Electronic phase diagram has been derived for the Prussian-Blue-type cyano-bridged transition-metal compound, \( \text{Na}_{0.84-\delta}\text{Co}[\text{Fe(CN)}_6]_{0.71-0.61} \cdot 3.8\text{H}_2\text{O} \) \((0 \leq \delta \leq 0.61)\), as a function of the hole concentration \( \delta \) of the \( d \)-electron system. The mother compound \((\delta=0)\) takes the \( \text{Co}^{2+} (t_{zg}^2) \cdot S=3/2 \) and \( \text{Fe}^{3+} (t_{zg}^5) \cdot S=0 \) configuration and is paramagnetic down to zero temperature. At room temperature, the holes are selectively introduced on the Fe site. A slight hole doping \((\delta=0.13)\) causes the charge-transfer (CT) transition, that is, cooperative electron transfer from the \( \text{Co}^{3+} \) site to the \( \text{Fe}^{3+} \) site, with a decrease in temperature below \( T_{\text{CT}} \approx 250 \text{ K} \). With a further increase in \( \delta \), \( T_{\text{CT}} \) slightly decreases from \( \approx 230 \text{ K} \) at \( \delta=0.24 \) to \( \approx 210 \text{ K} \) at \( \delta=0.61 \). Accordingly, the nature of the transition changes from the second-order type to the first-order type. In all the concentration ranges, the high-temperature (HT) phase is metastable even at low temperature. In this metastable phase, the \( \text{Fe}^{3+} (t_{zg}^5) \cdot S=1/2 \) species mediate the ferromagnetic exchange coupling between the adjacent \( \text{Co}^{3+} \) spins. The ferromagnetic transition appears at \( \delta=0.39 \), and the transition temperature \( T_c \) increase from \( 7 \text{ K} \) at \( \delta=0.39 \) to \( 13 \text{ K} \) at \( \delta=0.61 \). Based on these experimental data, we will discuss the significant roles of the coupling between the charge, spin, and lattice degrees of freedom in the transition-metal cyanides.

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I. INTRODUCTION

The phase diagram as a function of doping level \((x)\) frequently contributes to the deeper comprehension of the electronic systems and to the material design for realization of the unconventional physical properties as well as the giant response to the external stimuli. For example, in doped manganese, e.g., \( \text{Nd}_{1-x}\text{SrMnO}_3 \) the charge degree of freedom couples with the spin and orbital degrees of freedom and causes a variety of spin-charge-orbital ordered states.\(^1\) In the lightly doped region \((x \approx 0.48)\), \( \text{Nd}_{1-x}\text{SrMnO}_3 \) is ferromagnetic and metallic due to the double-exchange mechanism.\(^2\) In the vicinity of the half-doping \((x \approx \frac{1}{2})\), a charge-ordered phase appears below \( T_{\text{CO}} \approx 150 \text{ K} \) (Ref. 3) with \( d_{z^2-r^2}/d_{3z^2-r^2} \) as the orbital alternation. With further doping, the \( d_{z^2-r^2} \) \((d_{3z^2-r^2})\) orbital ordered phase appears at \( x \approx 0.52 \) \((x \approx 0.65)\). Such a successive phase change is well explained by the double-exchange model with explicitly including the orbital degree of freedom.\(^4\)\(^5\) The phase diagram of doped manganese stimulates the material scientists and triggers many findings.\(^1\)

The hole-doping procedure is also possible in the Prussian-Blue-type cyanido-bridged transition-metal compound, \( A_x[M'(\text{CN})_6]_y \cdot z\text{H}_2\text{O} \) \((A, M, M' \text{ are alkaline metal, transition metal, and transition metal, respectively})\). Crystallographically, the compound belongs to the face-centered cubic \((Fm\overline{3}m; Z=4)\), in which Co and Fe ions form a rocksalt-type \((\text{NaCl-type})\) network with sharing cyano \((\text{CN}^-)\) moieties—\(\text{CN-M-NC-M'--CN-M}^-\).\(^7\) The nanospaces formed by the network accommodate the alkaline metal ions \((A^+)\) and a part of water molecules \((\text{zerolite water})\). The residual water molecules \((\text{ligand water})\) occupy the vacancy of the \([M'(\text{CN})_6]_y\) site and coordinate with the \( A \) site. We can remove \( A \) from the nanospaces by an electrochemical method\(^8\) and introduce the holes on the \( d \)-electron system.\(^9\)

Among the cyano-bridged transition-metal cyanides, the Co-Fe compound is most extensively investigated because they show a charge-transfer (CT) transition from the high-temperature phase \([\text{Co}^{2+}(t_{zg}^2)\cdot\text{Fe}^{3+}(t_{zg}^5); \text{HT} \text{ phase}]\) to the low-temperature phase \([\text{Co}^{3+}(t_{zg}^5)\cdot\text{Fe}^{2+}(t_{zg}^3); \text{LT} \text{ phase}]\).\(^10\)

This CT transition accompanies a significant increase in the lattice constant \( a \) from \( \approx 9.9 \text{ Å} \) in the LT phase to \( \approx 10.3 \text{ Å} \) in the HT phase. The compound further shows the photoinduced magnetization\(^11\)\(^12\) as well as the photoinduced structural change.\(^13\) At low temperatures \((\approx 150 \text{ K})\), the photoexcitation induces the phase transition from the LT phase to the magnetic HT phase.\(^10\)\(^13\)

Sato et al.\(^11\) reported the enhancement of the magnetization in \( \text{K}_{0.1}\text{Co}[\text{Fe(CN)}_6]_{0.71-4.93\text{H}_2\text{O}} \) by irradiation of a red light \((660 \text{ nm})\) at \( 5 \text{ K} \) and suppression of the magnetization by irradiation of a blue light \((450 \text{ nm})\) at \( 5 \text{ K} \).

So far, Shimamoto et al.\(^10\) investigated the chemical composition effects on the CT transition in \( \text{Na}_x[\text{Co}[\text{Fe(CN)}_6]_{0.71-4.93\text{H}_2\text{O}} \) powders, which were synthesized by a solution reaction procedure with controlling the NaCl concentration and temperature. They find a systematic increase in the critical temperature \((T_{\text{CT}})\) for the CT transition with an increase in the NaCl concentration. The authors as-
scribed the increase in $T_C$ to the decrease in the vacancy concentration ($1-y$) of $[\text{Fe(CN)}]_6$ because it strengthens the ligand field at the Co site to stabilize the LT phase. The solution reaction procedure, however, alters not only $1-y$ but also the Na concentration ($x$) and water content ($z$). In addition, the obtained powders are not suitable for the optical measurement, especially for the time-resolved spectroscopy, due to the intense light scattering. These situations may discourage the quantitative argument on the experimental data.

In this paper, we have prepared a series of valence-controlled Co-Fe cyanide films, $\text{Na}_{0.84-x}\text{Co}[\text{Fe(CN)}]_6\cdot3.8\text{H}_2\text{O}$ ($0.0 \leq \delta \leq 0.61$), by an electrochemical method without changing vacancy concentration or the water content. Here, note that the parameter $\delta$ represents the concentration of the trivalent transition metal per a Co site: the chemical formula, $\text{Na}_{0.84-x}\text{Co}[\text{Fe(CN)}]_6\cdot3.8\text{H}_2\text{O}$, can be expressed as $\text{Na}^{+}_{0.84-x}\text{Co}^{3+}[\text{Fe}^{3+}(\text{CN})]_6\cdot3.8\text{H}_2\text{O}$ in the HT phase. In an analogy of the perovskite oxide system, we will call $\delta$ as “hole” concentration of the d-electron system. We have investigated the magnetic behavior of the films and derived the electronic phase diagram as a function of $\delta$. Based on these experimental data, we will discuss the significant roles of the coupling between the charge, spin, and lattice degrees of freedom. We further systematically investigated the absorption spectra in the infrared and visible region. Based on the systematic change of the visible absorption spectra, we have decomposed the spectra into four optical transitions.

II. EXPERIMENT

A. Sample preparation and characterization

Films of the $\text{Na}_{x}\text{Co}[\text{Fe(CN)}]_6\cdot3\text{H}_2\text{O}$ were electrochemically synthesized on the indium tin oxide (ITO) transparent electrodes (sheet resistances was 100 $\Omega$) under potentiostatic condition at 0.5 V versus a standard Ag/AgCl electrode in an aqueous solution containing 0.5 mmol/l $\text{K}_{x}\text{[Fe}^{3+}(\text{CN})]_6$, 1.25 mmol/l $\text{Co}^{3+}(\text{NO}_3)_2$, and 1 mol/l $\text{Na(NO}_3)$. We added saw-toothed-type modulation (±0.35 V and 71 Hz) to the applied potential. Before the film growth, the surface of the ITO electrode was purified by the electrolysis of water for several minutes. The obtained films were of transparent green. The elemental analysis by the inductively coupled plasma (ICP) method and CNH organic elementary analyzer (Perkin-Elmer 2400 CHN elemental analyzer) yields $\text{Na}_{0.84}\text{Co}[\text{Fe(CN)}]_{6.07}$·3.8H2O. The film thickness was about 1000 nm, which was determined by the cross-sectional image of the scanning electron microscope (SEM). The x-ray diffraction pattern revealed that the compound is face-centered cubic with lattice constant $a=10.251$ Å.

The hole concentration $\delta$ of the film was controlled by the oxidation process of the film at 0.5–0.7 V versus a standard Ag/AgCl electrode in 1 mol/l Na(NO3) aqueous solution. The as-grown films that were synthesized with the saw-toothed-type potential modulation are strongly (111) oriented, as revealed by the intense (111) Bragg reflection in the x-ray diffraction pattern. The orientation remains even after the oxidation process. We have investigated the film surface by SEM and found that the cubic crystals, whose size is ~100 nm, point their corners upward.

B. Structural and magnetic measurements

In order to investigate the structural properties of the hole-doped Co-Fe cyanide films, x-ray powder-diffraction patterns were measured at the synchrotron-radiation facility, SPring-8. First, the film was carefully removed from the ITO glass with a microspatula, and then the fine powders were filled into 0.5 mmol/l glass capillary. The capillary was sealed up and was put on a Debye-Scherrer camera at the BL02B2 beamline of SPring-8. The wavelength of the x-ray was 0.801 65 Å, which was calibrated by the lattice constant of standard CeO2 powders. The sample temperature was controlled by the cooled nitrogen gas. The exposure time was 5 min. The lattice parameters were refined by the Rietveld method with the face-centered-cubic ($Fm\bar{3}m; Z=4$) model.

The magnetic properties of the hole-doped films were investigated with superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). In order to reduce the background magnetic susceptibility, the film was carefully removed from the ITO glass with a microspatula, and then the fine powders were filled into 0.5 mmol/l glass capillary. The background signal from the glass capillary is order of 10⁻⁶ emu, which is two order smaller than the signal from the sample powders. The typical sample mass was ~100 $\mu$g, which was estimated from the film thickness and the removed area with assuming the ideal density. We are careful enough to seal the glass capillary to keep the circumstance even in the SQUID magnetometer.

C. Optical measurement

The absorption spectra in the infrared region were measured with the use of an infrared microscope system (JASCO ITR-3000) equipped with a Fourier-transform-type infrared spectrometer. The transmitted light was focused on a cooled HgCdTe infrared detector. We posted a scotch tape on the film surface to reduce the interference effect. The absorption spectra in the visible to violet were measured with a conventional monochromator system with a halogen lamp. The transmitted light was focused on a Si photodiode, and the lock-in detection was adopted to enhance the S/N ratio.

III. RESULTS

A. Valence control by an electrochemical method

We plotted in Fig. 1 the chemical composition of $\text{Na}_{x}\text{Co}[\text{Fe(CN)}]_{6}$·3H2O, that is, $x$, $y$, and $z$, as a function of the total charge $q$ used in the oxidation process. We emphasize that that $y$ (0.84) and $z$ (3.8) are constant under the oxidation process. The Na concentration ($x$) decreases in proportion to $q$: $x=0.84–0.86q$. So, we used the empirical relation between $q$ and $x$ to estimate $\delta=0.84–x$. Here, note that $\delta$ represents the concentration of the trivalent transition metal per a Co site: the chemical formula, $\text{Na}_{0.84-x}\text{Co}[\text{Fe(CN)}]_{6.07}$·3.8H2O, can be expressed as
First, let us investigate the temperature dependence of the magnetic susceptibility \( \chi \) on thin films of \( \text{Na}_{0.84-}\alpha \text{Co[Fe(CN)]}_{0.71} \cdot 3.8\text{H}_2\text{O} \). In Fig. 4, we show prototype examples of \( \chi T \) against temperature \( T \): (a) \( \delta=0.00 \), (b) \( \delta=0.24 \), and (c) \( \delta=0.61 \). The black curves were obtained in the cooling run under a magnetic field of 5000 G, while the gray curves were obtained in the warming run after the quench procedure at 5 K. In the as-grown film [(a) \( \delta=0.00 \)], the \( \chi T-T \) curve shows the Curie-type behavior (the black and red curves are completely overlapped). The estimated effective moment \( \mu_{\text{eff}}(=4.03 \mu_B/\text{Co}) \) is close to the ideal value \( (\approx 3.87 \mu_B/\text{Co}) \) for the high-spin Co\(^{2+}\) ions.

In the fully hole-doped sample [(c) \( \delta=0.61 \)], several transitions are observed. Here, we emphasize that the chemical...
FIG. 4. (Color online) Temperature dependence of $\chi T$ (where $\chi$ and $T$ are susceptibility and temperature) of thin films of Na$_{0.84}$Co[Fe(CN)$_{6}$]$_{0.71}$·3.8H$_{2}$O: (a) $\delta=0.00$, (b) $\delta=0.24$, and (c) $\delta=0.61$. The black curves were obtained in the cooling run under a magnetic field of 5000 G, while the gray curves were obtained in the warming run after the quench procedure at 5 K. $T_m$ and $T_{CT}$ represent the critical temperature of the CT transition and the melting temperature of the metastable phase.

FIG. 5. (a) Lattice constant $a$ at 300 K ($\approx T_{CT}$) and at 100 K ($\approx T_{HT}$) of thin films of Na$_{0.84}$Co[Fe(CN)$_{6}$]$_{0.71}$·3.8H$_{2}$O against $\delta$. (b) $\mu_{eff}^{LT}/\mu_{eff}^{HT}$ against $\delta$, where $\mu_{eff}^{LT}$ ($\mu_{eff}^{HT}$) is the effective moment in the LT (HT) phase. (c) Electronic phase diagram of thin films of Na$_{0.84}$Co[Fe(CN)$_{6}$]$_{0.71}$·3.8H$_{2}$O against $\delta$. The curves in (a) and (c) are merely the guide to the eyes. The curve in (b) is the calculation (see text).

Thus obtained $T_{CT}$ is plotted in Fig. 5(c) against $\delta$. A slight hole doping ($\delta=0.13$) causes the CT transition at $T_{CT}$ = 250 K. With a further increase in $\delta$, $T_{CT}$ slightly decreases from $\approx 230$ K at $\delta=0.24$ to $\approx 210$ K at $\delta=0.61$. The weak correlation between $T_{CT}$ and $\delta$ supports the idea that $T_{CT}$ is mainly governed by the magnitude of the ligand field around the Co site.$^{[10,23]}$ Nevertheless, the nature of the transition changes from the second-order type without thermal hysteresis to the first-order type with significant hysteresis.

In Fig. 5(a), we plotted the lattice constant $a$ at 300 K ($\approx T_{CT}$) and at 100 K ($\approx T_{HT}$), which were determined from the synchrotron-radiation x-ray powder-diffraction patterns. The conventional thermal contraction of $a$ is negligible, as seen in the nondoped compound ($\delta=0.00$). The magnitude of the lattice-constant change ($\Delta a$) at the CT transition seems to correlate with the nature of the transition; the larger $\Delta a$ becomes, the larger the thermal hysteresis becomes. The slight reduction in $T_{CT}$ with $\delta$ may be ascribed to the increase in $a$ at 300 K because it weakens the ligand field around the Co site to stabilize the HT phase.

Here, let us consider the ratio of the charge-transferred Co site at the CT transition. If the charge transfer takes place between the Fe$^{3+}$-Co$^{2+}$ pairs, the spin species of the system changes from Co$^{2+}$ ($S=3/2$: density is 1) and Fe$^{3+}$ ($S=1/2$: $\delta$ to Co$^{2+}$ ($S=3/2$: $1-\delta$). Then, the magnitude of $\mu_{eff}$ decreases below $T_{CT}$, and the ratio $\mu_{eff}^{LT}/\mu_{eff}^{HT}$ is expressed as

$$\frac{\mu_{eff}^{LT}}{\mu_{eff}^{HT}} = \sqrt{\frac{15(1-\delta)}{15+3\delta}},$$

where $\mu_{eff}^{LT}$ ($\mu_{eff}^{HT}$) is the effective moment in the LT (HT) phase. In Fig. 5(b), we plotted experimentally obtained $\mu_{eff}^{LT}/\mu_{eff}^{HT}$ together with the above calculation. The calcula-
ELECTRONIC PHASE DIAGRAM OF VALENCE-COOLED...  PHYSICAL REVIEW B 77, 224436 (2008)

C. Magnetic phase diagram of the quenched phase

Now, let us proceed to the magnetic properties of the quenched HT phase. In this phase, the spin species are Co$^{2+}$ ($S=3/2$; density is 1) and Fe$^{3+}$ ($S=1/2$; δ). Then, the ferromagnetic coupling between the neighboring Co spins can be mediated by the antiferromagnetic superexchange coupling between the Co$^{2+}$ and Fe$^{3+}$. In the inset of Fig. 6, we show temperature variation of the spontaneous magnetization $M_0$. In this measurement, the sample was cooled down to 2 K in the field of 5000 G. Then, $M_0$ was measured in the warming run in the zero field after the sample was cooled down to 2 K in the field of 5000 G.

D. Electronic structure

Figure 7 shows the visible absorption spectra of the films at 300 K: (a) δ=0.00, (b) δ=0.39, and (c) δ=0.61. In the as-grown film [(a) δ=0.00], an intense absorption band is observed at 3.3 eV (A band) together with the weak absorptions around 2 eV (D and E bands). The D and E bands can be ascribed to the intra-atomic $d-d$ transition of Co$^{2+}$. Such a $d-d$ transition is dipole-forbidden within a centrosymmetric (O$_h$) ligand field, that is, Co[Fe(CN)$_6$]$_2_4$. In an actual system, however, parts of the [Fe(CN)$_6$]$_2$ site are replaced by the ligand water. Then, the resultant asymmetric ligand field allows the $d-d$ transition via the strong hybridization between the Co$_{ef}$ orbital and the CN$^{-\alpha}$ orbital. Actually, Ohkoshi et al. reported a similar 2.0 eV band in (Co$_{0.41}$Mn$_{0.59}$)[Cr$^{III}$$(CN)$_6$]$_2$4.2H$_2$O and ascribed it to the intra-atomic $d-d$ transition of Co$^{2+}$. In the fully hole-doped sample [(c) δ=0.61], three optical transitions, that is, 2.4 eV (CT band), 3.1 eV (B band), and 3.7 eV (C band), are observed. Among them, the lowest-lying band (CT band) is ascribed the electron transfer from the Co$^{2+}$ site to the Fe$^{3+}$ site.

We decomposed the absorption spectra $\alpha(\omega)$ into the four absorption bands,

$$\alpha(\omega) = \sum_{i=A,B,C,CT} \frac{S_i}{2\pi} \exp \left( - \frac{(\hbar \omega - \hbar \omega_i)^2}{2\Gamma_i^2} \right),$$

where $S_i$, $\hbar \omega_i$, and $\Gamma_i$ are the spectral weight, the resonant energy, and the spectral width, respectively. In the fitting procedure, we fixed the values of $\omega_i$ and $\Gamma_i$ and adjusted magnitude of $S_i$. The thin solid curves in Fig. 7 are the least-squares-fitted results. In Fig. 8, we plotted the oscillator strength $f$ for these absorption bands against $\delta$. The magnitude of $f$ of the A band linearly decreases with $\delta$, while those of the B, C, and CT bands linearly increase. These $\delta$-dependent behavior indicate that the A band (the B, C, and CT bands) should relate to the Fe$^{2+}$ (Fe$^{3+}$) species. Especially, the linear increase in $S_{CT}$ with $\delta$ is consistent with its
assignment, that is, Fe$^{3+}$→Co$^{2+}$. On the other hand, the higher-lying A band (B and C bands) can be ascribed to the intermolecular transition of [Fe$^{3+}$(CN)$_6$]$_2$ ([Fe$^{3+}$(CN)$_6$]). We ascribe the B band (the C band) to the electron transfer from CN$^-$ to the unoccupied t$_{2g}$(e$_g$) orbital of Fe$^{3+}$ because the energy splitting (≈0.58 eV) is reasonable for the crystal-field splitting. In Table I, we listed the parameters of the optical transitions together with the assignment. We note that the magnitude of $f$=(0.06/Fe) for the CT transition is comparable to that (≈0.03/Mn) for the J$_g$-gap transition (electron transfer between the neighboring Mn sites) of La$_{0.6}$Sr$_{0.4}$MnO$_3$.25

IV. DISCUSSION

In this section, we will discuss the $\delta$ dependence of the CT transition. Before the discussion, let us summarize the important items observed in the present experiment. First of all, we found that the correlation between $T_{CT}$ and $\delta$ is quite weak [see Fig. 5(c)]. This suggests that $T_{CT}$ is mainly governed by the magnitude of the ligand field around the Co site. Second, the ratio of the charge-transferred Co site at the CT transition is $\delta$, as confirmed by the $\delta$ dependence of $\mu_{eff}/\mu_{eff}^{HT}$ [see Fig. 5(b)]. Third, we found that the CT transition accompanies the significant reduction in $a$ even at $\delta$=0.13 [see Fig. 5(a)]. This observation strongly suggests that the CT transition is cooperative and uniform, even when a small part of the Co site is charge-transferred. Here, we emphasize that significant reduction of the Co-Fe bond distance is indispensable to stabilize the charge-transferred state, that is, Fe$^{2+}$-Co$^{3+}$. Actually, the bond distance decreases from 5.17 to 5.02 Å at the CT transition in the fully hole-doped sample ($\delta$=0.61). Such a bond compression should be ascribed to the concomitant spin state transition of Co$^{3+}$ into the low-spin state ($t_{2g}^6$). In this sense, the strong coupling between the charge, spin, and lattice degrees of freedom is the key of the CT transition.

In Fig. 9, we show schematic illustrations of the hole-doped Co$^{2+}$-Fe$^{2+}$ system. In larger-$\delta$ region [Fig. 9(c)], most of the Fe sites have holes and can transfer an electron to the neighboring Co site. The charge-transfer process accompanies the significant Co-Fe bond compression. The bond compressions should take place cooperatively in order to minimize the distortion energy of the lattice system. As a result, $a$ in the LT phase becomes much shorter than that in the HT phase, causing a high potential barrier between the two phases. Then, the nature of the CT transition in large-$\delta$ region is of first-order, as observed in Fig. 5(c).

In small-$\delta$ region [Fig. 9(b)], however, only a small part of the Fe site has hole. Nevertheless, the uniform CT transition suggests that the local lattice distortions induced by the charge transfer are weakly connected all over the system in a percolation manner. In such a situation, the lattice-constant change ($\Delta a$) at the CT transition should be suppressed as

![FIG. 8. Oscillator strength $f$ of thin films of Na$_{0.84-\delta}$Co[Fe(CN)$_6$]$_{0.71}$:3.8H$_2$O at 300 K. The straight lines are the least-squares-fitted results.](image)

![FIG. 9. Schematic illustrations of hole-doped Co$^{2+}$-Fe$^{2+}$ system: (a) $\delta$=0, (b) small $\delta$, and (c) large $\delta$. Circles and squares represent the Fe and Co site, respectively. White color indicates the hole site (Fe$^{3+}$).](image)

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<td>A</td>
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<td>0.10/Fe$^{2+}$</td>
<td>CN$^-$→Fe$^{2+}$ or Fe$^{2+}$→CN$^-$</td>
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<tr>
<td>B</td>
<td>3.14</td>
<td>0.07/Fe$^{3+}$</td>
<td>CN$^-$→Fe$^{3+}t_{2g}$</td>
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<tr>
<td>C</td>
<td>3.72</td>
<td>0.03/Fe$^{3+}$</td>
<td>CN$^-$→Fe$^{3+}e_g$</td>
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<tr>
<td>CT</td>
<td>2.41</td>
<td>0.06/Fe$^{3+}$</td>
<td>Co$^{2+}$→Fe$^{3+}$</td>
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<tr>
<td>D</td>
<td>1.99</td>
<td>0.002/Co</td>
<td>d→d within Co$^{3+}$</td>
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<tr>
<td>E</td>
<td>2.18</td>
<td>0.003/Co</td>
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ELECTRONIC PHASE DIAGRAM OF VALENCE-
GION TO THE FIRST-ORDER TYPE IN THE LARGE-
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however, changes from second-order type in the small-
TION OF THE HOLE CONCENTRATION *Author to whom correspondence should be addressed; moritomo@sakura.ac.jp

V. SUMMARY

We have derived the electronic phase diagram as a func-
tion of the hole concentration $\delta$ for thin films of $\text{Na}_{x}\text{Co}_{1-x}\text{Fe(CN)}_{6} \cdot 3.8\text{H}_{2}\text{O} (0.0 \leq \delta \leq 0.61)$. We ob-
served the cooperative CT transition in the wide concentra-
range of $0.13 \leq \delta \leq 0.61$. The nature of the CT transition, however, changes from second-order type in the small-$\delta$ re-
gion to the first-order type in the large-$\delta$ region. The $\delta$ de-
pendence of the CT transition was discussed in terms of the

coupling between the charge, spin and lattice degrees of free-
dom. Here, we emphasize that only a small part of the charge
transfer can trigger the cooperative phase transition in the
present Co-Fe cyanide system. This implies that even the
partial charge-transfer induced by photoexcitation may cause
a cooperative phase transition. Investigation on this trend is
now in progress.

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