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

Nakada F., Kamioka H., Moritomo Y., Kim J. E., Takata M.

*Physical Review B*

Volume 77

Number 22

Pages 224436

(C)2008 The American Physical Society

URL: http://hdl.handle.net/2241/100083

doi: 10.1103/PhysRevB.77.224436

| 著者 | 坂田 哲, 鎌岡 浩, 森本 野, 金 浩, 高田 
| 電子図書館 | | |
| 論文書名 | オレグマウス電子分極図の検討 - リストリート研究への影響 |
| 権利 | 本資料の複製及び公衆送信権を有します |

| 資料 | 本資料の複製及び公衆送信権を有します |

| 資料 | 本資料の複製及び公衆送信権を有します |
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 manganite, e.g., $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, the charge degree of freedom couples with the spin and orbital degrees of freedom and causes a variety of spin-charge-orbital ordered states. In the vicinity of the half-doping ($x=0.48$), $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ is ferromagnetic and metallic due to the double-exchange mechanism. In the lightly doped region ($x \leq 0.48$), $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ is ferromagnetic and metallic due to the double-exchange mechanism. 1

The hole-doping procedure is also possible in the Prussian-Blue-type cyano-bridged transition-metal compound, $\text{AxM}[^{\text{M}}/\text{H}_2\text{O}]$. The 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 (NaCl-type) network with sharing cyanido ($\text{CN}^-$) moieties—$\text{CN}-\text{M}-\text{NC}-\text{M}^-'-\text{CN}$. The nanospaces formed by the network accommodate the alkaline metal ions ($\text{A}^+$) and a part of water molecules (zerolite water). The residual water molecules (ligand water) occupy the vacancy of the $[\text{M}^{\text{II}}/\text{CN}]_3$ site and coordinate with the $\text{M}$ site. We can remove $\text{A}$ from the nanospaces by an electrochemical method and introduce the holes on the $d$-electron system. 2

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 $[\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}; \text{CN}^{\text{-}}; \text{H}_2\text{O}]$ to the low-temperature phase $[\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}; \text{CN}^{\text{-}}; \text{H}_2\text{O}]$. 3

This CT transition accompanies a significant increase in the lattice constant $a$ from $\approx 9.9$ Å in the LT phase to $\approx 10.3$ Å in the HT phase. The compound further shows the photoinduced magnetization, as well as the photoinduced structural change. 4 At low temperatures ($\leq 150$ K), the photoexcitation induces the phase transition from the LT phase to the magnetic HT phase. 5

Sato et al. reported the enhancement of the magnetization in $\text{K}_{0.1}\text{Co[Fe(CN)}]_{0.71} \cdot 4.93\text{H}_2\text{O}$ 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.

So far, Shimamoto et al. investigated the chemical composition effects on the CT transition in $\text{Na}_x\text{Co[Fe(CN)}]_{3-x} \cdot 3\text{H}_2\text{O}$ 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 [Fe(CN)$_6$]$^{3−}$ 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, $\text{Na}_{0.84−x}\text{Co[Fe(CN)$_6$]}_{0.71−y}\cdot3.8\text{H}_2\text{O}$ (0.0 ≤ $\delta$ ≤ 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, $\text{Na}_{0.84−x}\text{Co[Fe(CN)$_6$]}_{0.71−y}\cdot3.8\text{H}_2\text{O}$, can be expressed as $\text{Na}^{+}_{x}\text{Co}^{3+}[\text{Fe}^{2+}(\text{CN})]_{6}^{-}\cdot3.8\text{H}_2\text{O}$ 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 $\text{Na}_{x}\text{Co[Fe(CN)$_6$]}_{1−x}\cdot3\text{H}_2\text{O}$ were electrochemically synthesized on the indium tin oxide (ITO) transparent electrodes (sheet resistances was 100 Ω) under potentiostatic condition at 0.5 V versus a standard Ag/AgCl electrode in an aqueous solution containing 0.5 mol/l $K_{2}[\text{Fe}^{3+}(\text{CN})]_{6}$, 1.25 mmol/l Co(NO$_3$)$_2$ and 1 mol/l Na(NO$_3$)$_2$. 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 $\text{Na}_{x}\text{Co[Fe(CN)$_6$]}_{1−x}\cdot3\text{H}_2\text{O}$. 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(NO$_3$)$_2$ 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 mm$^3$ glass capillaries. 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 CeO$_2$ 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 (Fm3m; 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 mm$^3$ glass capillaries. 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 $\text{Na}_{x}\text{Co[Fe(CN)$_6$]}_{1−x}\cdot3\text{H}_2\text{O}$, 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, $\text{Na}_{0.84−x}\text{Co[Fe(CN)$_6$]}_{0.71−y}\cdot3.8\text{H}_2\text{O}$, can be expressed as
The magnitude of $f$ for the [Fe(II)(CN)$_6$] band linearly decreases with $\delta$, while that for the [Fe(II)(CN)$_6$] band linearly increases. This clearly indicates that the holes are introduced on the Fe site at 300 K. It is interesting that the absolute magnitude of $f(=1.1 \times 10^{-3}$/CN) for the [Fe(II)(CN)$_6$] band is much larger than that ($f(=0.4 \times 10^{-3}$/CN) for the [Fe(II)(CN)$_6$] band. This may reflect the different bonding electron distribution between [Fe(II)(CN)$_6$] and [Fe(II)(CN)$_6$], which is recently revealed by the maximum entropy method charge-density analysis.\(^{19}\)

### B. Electronic phase diagram

First, let us investigate the temperature dependence of the magnetic susceptibility $\chi$ on thin films of Na$_{0.84-x}$Co[Fe(CN)$_6$]$_{0.71}$-3.8H$_2$O. In Fig. 4, we show proto-

**FIG. 3.** Oscillator strength $f$ of the CN stretching vibration of [Fe(II)(CN)$_6$] and [Fe(II)(CN)$_6$] at 300 K. The straight lines are the least-squares-fitted results.
procedure

further increase in temperature, the CT transition from the corresponding anomalies due to the CT transition and the powders. With a decrease in temperature from 300 K to 187 K. The reduction corresponds to the CT transition from the metastable phase into the LT phase. Here we represent the critical temperature of the CT transition and the melt 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 ($<T_{CT}$) and at 100 K ($<T_{CT}$), 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$^{3+}$ ($S=3/2$; $1-\delta$). Then, the magnitude of $\mu_{eff}$ decreases below $T_{CT}$, and the ratio $\mu_{eff}^{LT}/\mu_{eff}^{HT}$ is expressed as

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

where $\mu_{eff}^{LT}$ 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 POLYCRYSTALLINE Na0.84−δCo[Fe(CN)6]0.71·3.8H2O AGAINST δ. The inset shows temperature variation of the spontaneous magnetization Mt. Mt 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.

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 Co3+ (S=3/2; density is 1) and Fe3+ (S=1/2; δ). Then, the ferromagnetic coupling between the neighboring Co spins can be mediated by the antiferromagnetic superexchange coupling between the Co2+ and Fe3+. In the inset of Fig. 6, we show temperature variation of the spontaneous magnetization Mt. In this measurement, the sample was cooled down to 2 K in the field of 5000 G. Then, Mt was measured in the warming run in the zero field. Above δ=0.39, we observed finite Mt value. The Curie temperature Tc increases with δ; Tc=7 K and Tc=10 K at δ=0.50 and Tc=13 K at δ=0.61.

Thus obtained Tc (open circle) is plotted in Fig. 6 together with the melting temperature Xm (filled circle). With the increase in δ beyond ~0.3, Tc suddenly appears and then gradually increases. Such a behavior of Tc can be explained by the percolation theory. The introduced Fe3+ site mediated the ferromagnetic couplings among the surrounding six Co spins, causing a small ferromagnetic cluster of the Co site. The size of the ferromagnetic cluster increases with δ. The percolation theory tells us that the cluster size becomes infinite if δ exceeds a critical value δc [%0.195 (Ref. 22)] for the face-centered-cubic lattice.

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 Co2+. Such a d-d transition is dipole-forbidden within a center-symmetric (O2) ligand field, that is, Co[Fe(CN)6]2+. In an actual system, however, parts of the [Fe(CN)6]3− site are replaced by the ligand water. Then, the resultant asymmetric ligand field allows the d-d transition via the strong hybridization of the Coeg orbital and the CNσ* orbital. Actually, Ohkoshi et al. reported a similar 2.0 eV band in [CoII0.41MnII0.59][CrIII(CN)6]2−·4.2H2O and ascribed it to the intra-atomic d-d transition of Co2+. 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 Co2+ site to the Fe3+ site.10,14,15

We decomposed the absorption spectra α(ω) into the four absorption bands,

\[ α(ω) = \sum_{i=A,B,C,CT} S_i \exp \left( -\frac{(hω_i - hω)^2}{2Γ_i^2} \right), \]

where S_i, hω_i and Γ_i are the spectral weight, the resonant energy and the spectral width, respectively. In the fitting procedure, we fixed the values of ω_i and W_i and adjusted magnitude of S_i. The 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 δ. The magnitude of f of the A band linearly decreases with δ, while those of the B, C, and CT bands linearly increase. These δ-dependent behavior indicate that the A band (the B, C, and CT bands) should relate to the Fe2+ (Fe3+) species. Especially, the linear increase in S_CT with δ is consistent with its
ascribe the B band. On the other hand, the higher-lying A band (B and C bands) can be ascribed to the intermolecular transition of $[\text{Fe}^{3+}(\text{CN})_6] ([\text{Fe}^{3+}(\text{CN})_6])$. We ascribe the B band (the C band) to the electron transfer from $\text{CN}^-$ to the unoccupied $t_2g(e_g)$ orbital of Fe$^{3+}$ because the energy splitting ($\approx 0.58$ 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 $f(=0.06/\text{Fe})$ for the CT transition is comparable to that ($=0.03/\text{Mn}$) for the $J_g$-gap transition (electron transfer between the neighboring Mn sites) of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$.\textsuperscript{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 $T_{\text{CT}}$ and $\delta$ is quite weak [see Fig. 5(c)]. This suggests that $T_{\text{CT}}$ 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 $\mu_{\text{eff}}$ [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$^{3+}$-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. 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 $\text{Na}_{0.84-\delta}\text{Co}[\text{Fe}(\text{CN})_6]_{0.71} \cdot 3.8\text{H}_2\text{O}$ at 300 K. The straight lines are the least-squares-fitted results.](image)

**TABLE I.** Resonance energy $\hbar\omega$ and oscillator strength $f$ of the optical transitions of $\text{Na}_{0.84-\delta}\text{Co}[\text{Fe}(\text{CN})_6]_{0.71} \cdot 3.8\text{H}_2\text{O}$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\hbar\omega$ (eV)</th>
<th>$f$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.26</td>
<td>0.10/Fe$^{2+}$</td>
<td>CN$^-\rightarrow$Fe$^{2+}$ or Fe$^{2+}\rightarrow$CN$^-$</td>
</tr>
<tr>
<td>B</td>
<td>3.14</td>
<td>0.07/Fe$^{3+}$</td>
<td>CN$^-\rightarrow$Fe$^{3+}t_{2g}$</td>
</tr>
<tr>
<td>C</td>
<td>3.72</td>
<td>0.03/Fe$^{3+}$</td>
<td>CN$^-\rightarrow$Fe$^{3+}e_g$</td>
</tr>
<tr>
<td>CT</td>
<td>2.41</td>
<td>0.06/Fe$^{3+}$</td>
<td>Co$^{2+}\rightarrow$Fe$^{3+}$</td>
</tr>
<tr>
<td>D</td>
<td>1.99</td>
<td>0.002/Co</td>
<td>$d-d$ within Co$^{3+}$</td>
</tr>
<tr>
<td>E</td>
<td>2.18</td>
<td>0.003/Co</td>
<td>$d-d$ within Co$^{2+}$</td>
</tr>
</tbody>
</table>

![FIG. 9. Schematic illustrations of hole-doped Co$^{3+}$-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$^{2+}$).](image)
compared with that in large-\(\delta\) region. The suppressed \(\Delta\alpha\) causes the second-order nature of the phase transition.

V. SUMMARY

We have derived the electronic phase diagram as a function of the hole concentration \(\delta\) for thin films of \(\text{Na}_{0.84}^{1-\delta}\text{Co[Fe(CN)}_{6}^{2-}\cdot3\text{H}_{2}\text{O}\) \(\left(0.0 \leq \delta \leq 0.61\right)\). We observed the cooperative CT transition in the wide concentration range of \(0.13 \leq \delta \leq 0.61\). The nature of the CT transition, however, changes from second-order type in the small-\(\delta\) region to the first-order type in the large-\(\delta\) region. The \(\delta\) dependence of the CT transition was discussed in terms of the coupling between the charge, spin and lattice degrees of freedom. 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.

ACKNOWLEDGMENTS

This work was supported by a Grant-In-Aid for Scientific Research from the Ministry of Education, Culture, Sports and Science, Japan and from the Support Center for Advanced Telecommunication (SCAT) Foundation.