# Transparent and Colored Magnetic Thin Films: $(Fe^{II}_{x}Cr^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]$

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Prussian blue, $Fe_4[Fe(CN)_6]_3{\cdot}zH_2O$, is a well-known compound with an extensive history over the past 250 years. This compound shows a blue color and has been used as a dyeing material. Its analogues[1] show various physical properties such as electrochromism[2] and magnetism.[3] Particularly, interesting magnetic properties have been reported recently. For example, Verdaguer et al. reported a critical temperature of 315 K for the magnetic spin ordering with $V[Cr(CN)_6]_{0.86}{\cdot}2.8H_2O$.[3c] In addition, we found that $K_{0.2}Co^{III}_{1.4}[Fe^{II}(CN)_6]{\cdot}6.9H_2O$ shows a photoinduced reversible magnetization.[4] Usually, Prussian blue analogues incorporate only two types of metal ions. In the series of our work, we are trying to add new physical properties and functionality to prussian blue analogues by the strategy to incorporate three types of metal ions. The first example along this line was the compounds in the series of mixed ferro-ferrimagnet $(Ni^{II}_{x}Mn^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]{\cdot}7.5H_2O$ *powders* ($0 \leq x \leq 1$), manipulating both ferromagnetic ($J > 0$) and antiferromagnetic ($J < 0$) exchange interactions.[5] Moreover, in a mixed ferro-ferrimagnet $(Fe_{0.40}Mn_{0.60})_{1.5}[Cr^{III}(CN)_6]{\cdot}7.5H_2O$ *powder*, we have succeeded in demonstrating a novel photoinduced magnetic pole inversion.[6,7] The objective of the present work is to design various colored transparent magnetic thin films. The key to this strategy is to control of the intervalence transfer bands of metal ions in a dyeing material exhibiting ferromagnetism. We have prepared the new classes of transparent magnetic thin *films* composed of $(Fe^{II}_{x}Cr^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]{\cdot}zH_2O$. Their colors could be controlled by controlling the compositional factor $x$ ($= Fe^{II}/(Fe^{II} + Cr^{II})$), e.g., colorless ($x = 0$), violet ($x = 0.20$), red ($x = 0.42$), and orange ($x = 1$). The strategy of this work is essentially different from that of the electrochromism. Moreover, their magnetic properties are also rich in variety depending on $x$, e.g., disappearance of saturation magnetization, compensation temperatures, and anomalous coercive fields.

The mixed ferro-ferrimagnetic thin films composed of $(Fe^{II}_{x}Cr^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]{\cdot}zH_2O$ were prepared by reducing aqueous solutions containing three compounds ($K_3[Cr(CN)_6]$, $CrCl_3$, and $FeCl_3$), where the mixing ratio $x_{mix}$ ($= Fe^{III}/(Fe^{III} + Cr^{III})$) was controlled (Figure 1a). When we kept the reduction potential at −0.84 V vs SCE and loaded electrical capacity of 600 mC, insoluble polynuclear metal cyanides thin films with a thickness of ca. 2 $\mu$m were thus deposited on an electrode surface as thin films. The elemental analyses for these films showed that the experimentally obtained $x$ values depended on the $x_{mix}$ values of metal ions in the prepared solutions, e.g., $x = 0.04$ ($x_{mix} = 0.05$), $x = 0.08$ ($x_{mix} = 0.10$), $x = 0.11$ ($x_{mix} = 0.13$), $x = 0.13$ ($x_{mix} = 0.15$), $x = 0.20$ ($x_{mix} = 0.20$), $x = 0.31$ ($x_{mix} = 0.30$), and $x = 0.42$ ($x_{mix} = 0.40$).[8] The X-ray powder diffraction patterns for all the films were consistent with the fcc structure. The lattice constants increased successively from 10.39 to 10.62 Å with increasing $x$. Moreover, the CN stretching frequencies in the IR spectra for the films decreased continuously from 2189 to 2161 $cm^{-1}$.

The $x$ values of the $(Fe^{II}_{x}Cr^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]{\cdot}zH_2O$ series could be also controlled by tuning the electrode potential of reducing aqueous solutions containing $K_3[Cr(CN)_6]$, $CrCl_3$, and $FeCl_3$, e.g., $x = 0.25$ (−750 mV vs SCE in prepared solution for the $x_{mix} = 0.14$), $x = 0.15$ (−800 mV), $x = 0.13$ (−840 mV), $x = 0.11$ (−880 mV), $x = 0.09$ (−920 mV), and $x = 0.07$ (−980 mV). This is rationally explained to be due to the increase of distribution ratio of $Cr^{II}$ ion by raising the reduction potential.

Magnetic susceptibility and magnetization of obtained thin films depended strongly on the $x$ values. The saturation magnetizations ($I_s$) for $x = 0$ and $x = 1$ at fields up to 5 T, assuming $g = 2$ for metal ions, were determined to be 1.04 $\mu_B$ and 6.69 $\mu_B$, respectively. Those for the intermediate compositions varied in a systematic fashion as a function of $x$. Minimum values of the $I_s$ were found with the film of $x$ value close to 0.11. This is because parallel spins ($Cr^{III}$ and $Fe^{II}$) and antiparallel spins ($Cr^{II}$) can be partially or even completely canceled, depending on the $x$. Moreover, the coercive field $H_c$ for $x = 0.11$ was much larger than those at the other $x$ values, e.g., 6 G ($x = 0$), 3500 G ($x = 0.11$), and 150 G ($x = 1$) (Figure 1b). Because the atomic force microscopy images showed that the particle sizes of deposited crystals for the whole $x$ range were almost the same (200−300 nm diameter), the $H_c$ values are theoretically expected to be proportional to $(I_s)^{-1}$. Therefore, the $H_c$ value at minimum $I_s$ value should become to be the largest. In addition, the magnetization vs temperature curves below $T_c$ exhibited various types of behavior depending on $x$ (field = 10 G) (Figure 1c). Particularly, those compounds in which $x$ were 0.11−0.15 exhibited negative values of magnetization below particular temperatures (compensation temperatures, $T_{comp}$).[9] The $T_{comp} = 110$ K was recorded for $x = 0.15$. This $T_{comp}$ value is the highest value among molecule- or molecular-based magnets.[10] These temperature dependences

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(8) Elemental Analyses. Calcd for $Cr^{II}_{1.5}[Cr^{III}(CN)_6]{\cdot}7.5H_2O$: Cr, 30.8; C, 17.1; N, 20.0. Found: Cr, 30.5; C, 17.1; N, 20.0. Calcd for $(Fe^{II}_{0.42}Cr^{II}_{0.58})_{1.5}[Cr^{III}(CN)_6]{\cdot}7.5H_2O$: Fe, 8.3; Cr, 22.9; C, 17.0; N, 19.8. Found: Fe, 8.5; Cr, 22.9; C, 16.8; N, 20.0. Calcd for $Fe^{II}_{1.5}[Cr^{III}(CN)_6]{\cdot}8H_2O$: Fe, 19.2; Cr, 11.9; C, 16.5; N, 19.3. Found: Fe, 19.2; Cr, 11.3; C, 16.6; N, 19.2. Under our typical experimental conditions (humidity 70%, temperature 25 °C), $z$ was between 7 and 8.

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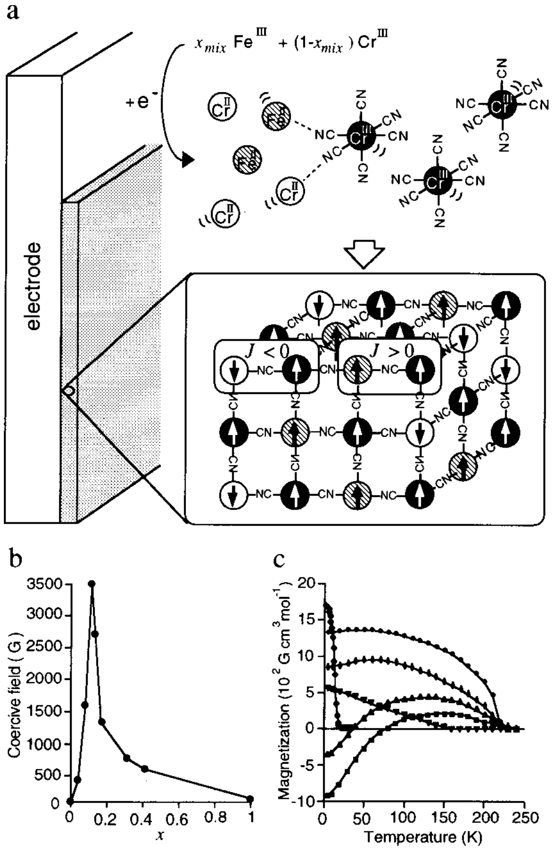

**Figure 1.** (a) Schematic diagram illustrating electrochemical synthesis of magnetic thin films with both ferromagnetic ($J > 0$) and antiferromagnetic ($J < 0$) interactions. Cr$^{III}$ (black spheres) and either Fe$^{II}$ (shaded spheres) or Cr$^{II}$ (white spheres), which are randomly incorporated in the lattice, are linked in an alternating fashion. (b) Plots of $H_c$ values versus $x$. (c) Magnetization vs temperature curves for (Fe$^{I}_{x}$Cr$^{II}_{1-x}$)$_{1.5}$[Cr$^{III}$(CN)$_6$]·zH$_2$O (field = 10 G): (●) $x = 0$; (♦) $x = 0.08$; (▲) $x = 0.11$; (■) $x = 0.13$; (▼) $x = 0.42$; (◆) $x = 1$.

could be qualitatively reproduced using molecular field theory, considering only two types of exchange couplings between nearest neighbor sites, one for Fe$^{II}$−Cr$^{III}$ ($J_{FeCr} = 0.9$ cm$^{-1}$) and the other for Cr$^{II}$−Cr$^{III}$ ($J_{CrCr} = -9.0$ cm$^{-1}$).[11] Therefore, these phenomena were observed because the positive magnetization due to the Cr$^{II}$ sublattice and the negative magnetizations due to the Fe$^{II}$ and Cr$^{III}$ sublattices have different temperature dependences.

The other interesting aspect of the obtained magnetic thin films is their optical properties. The colors of obtained (Fe$^{II}_{x}$Cr$^{II}_{1-x}$)$_{1.5}$[Cr$^{III}$(CN)$_6$]·zH$_2$O transparent films were changed depending on $x$. For example, the film for $x = 0$ was colorless, that for $x = 0.20$ was violet, that for $x = 0.42$ was red, and that for $x = 1$ was orange (Figure 2a). Their colors are due to the intervalence transfer (IT) band of Fe$^{II}$ and Cr$^{III}$ in the visible region,[1a,7] which is characteristic of mixed-valence compounds. As shown in Figure 2b, their IT bands shifted from short to long wavelengths in the visible region with decreasing $x$; e.g., $\lambda_{max} = 434$ nm ($x = 1$), 496 nm ($x = 0.42$), 506 nm ($x = 0.20$), and 510 and 610 nm ($x = 0$) and hence their films exhibited various types of color. In general, the wavelength of IT band depends on magnitudes of the vibronic coupling with asymmetrical distortion of each coordination sphere of metal ions and the intensity is proportional to the square of transfer integrals.[12] Therefore, in a series of

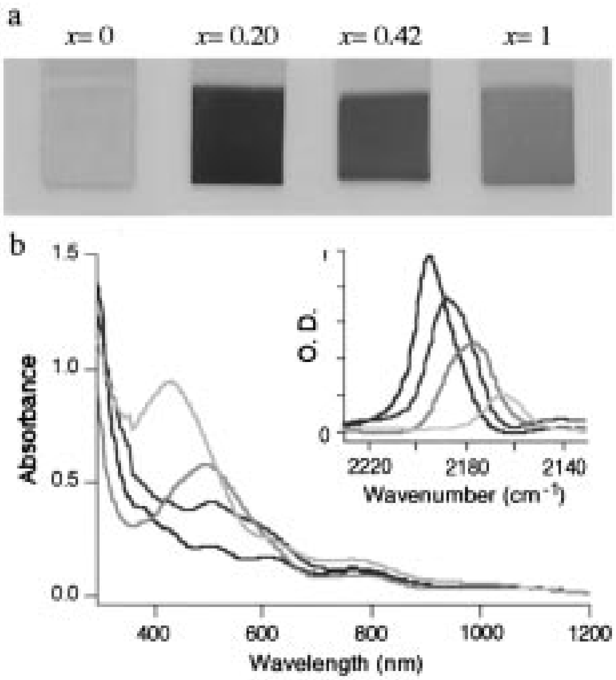

**Figure 2.** (a) The photographs of obtained transparent and colored magnetic thin films. (b) UV−vis and IR spectra of those: (black) $x = 0$; (violet) $x = 0.20$; (red) $x = 0.42$; (orange) $x = 1$. IR spectra are shown in the inset.

(Fe$^{II}_{x}$Cr$^{II}_{1-x}$)$_{1.5}$[Cr$^{III}$(CN)$_6$] films, magnitudes of vibronic coupling parameters and transfer integrals are supposed to be continuously changed from those of Fe$^{II}$-Cr$^{III}$ to those of Cr$^{II}$-Cr$^{III}$ with decreasing $x$. In fact, frequencies of CN stretching and lattice constants also continuously shifted, indicating that distance between metal ions of (Fe$^{II}_{x}$Cr$^{II}_{1-x}$)$_{1.5}$[Cr$^{III}$(CN)$_6$] are averaged values of the distance of Fe$^{II}$−Cr$^{III}$ and Cr$^{II}$−Cr$^{III}$ as a function of $x$.

In summary, we have succeeded in designing the various types of colored magnetic thin films composed of new types of prussian blue analogues incorporating three types of metal ions. Here, note that our strategy to tune color is essentially different from the electrochromism. Of course, when electrochemical reduction or oxidation of our thin films are performed on the electrode, each of thin films exhibits different types of color and magnetic properties furthermore, e.g., red ($x = 0.42$) versus dark blue at −1.0 V vs SCE. In general, the classical magnets show metallic luster or black. Here, note that even a yttrium iron garnet used as a photoisolater is seen to be black. Therefore, transparent and colored magnets will enable one to develop new types of functional thin films,[13,14] e.g., photothermal as well as photoinduced magnetic memory devices by choosing the types of laser color.

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