Design of a Novel Magnet Exhibiting Photoinduced Magnetic Pole Inversion Based on Molecular Field Theory

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Abstract: We show a novel magnetic phenomenon, “photoinduced magnetic pole inversion”, which occurs even in the absence of an external magnetic field. The key of this strategy is to control the compensation temperature by a pure photoprocess. Here, we combined two magnetic behaviors which were developed recently. One of them is the photoinduced change of magnetization for some of the Prussian blue analogues. The other is a so-called mixed ferro-ferrimagnetism in the system of ternary metal Prussian blue analogues. We show a strategy to obtain this phenomenon based on molecular field (MF) theory and we design new classes of ternary metal Prussian blue analogues, (Fe\textsuperscript{II},Mn\textsuperscript{II}–\textsuperscript{III})\textsubscript{5}[Cr\textsuperscript{III}(CN)\textsubscript{6}]\textsubscript{3}–\textsubscript{2}H\textsubscript{2}O, including photosensitive Fe\textsuperscript{II}–Cr\textsuperscript{III} sites. Their magnetic properties, such as saturation magnetization, coercive field, Curie temperature, and compensation temperature, were controlled by changing the compositional factor \(x\). When the material for \(x = 0.40\) was irradiated by visible light under a weak external magnetic field (10 G), the photoinduced magnetization reversal occurred. This phenomenon can be simulated well by the MF theory considering only two types of superexchange couplings between the nearest neighbor sites, one for Fe\textsuperscript{II}–Cr\textsuperscript{III} and the other for Mn\textsuperscript{II}–Cr\textsuperscript{III}.

I. Introduction

One of the targets in the field of magnetic materials is to develop new types of functionalized magnets. For example, magnetic materials exhibiting giant magnetic resistance effects open a new avenue in the field of magnetic memory devices.\textsuperscript{(1,2)} Our objective in the present work is to control magnetic magnetization in K\textsubscript{0.4} Co\textsubscript{II} 0.3 Co\textsubscript{III} [Fe\textsubscript{II} (CN)\textsubscript{6}] 7.5H\textsubscript{2}O.\textsuperscript{(3,4)} In this material, the spin states of Fe\textsubscript{II} (t\textsubscript{2g} 4 e\textsubscript{g} 2) and Co\textsubscript{III} (t\textsubscript{2g} 3) are not changed but the ferromagnetic coupling characteristics for this magnet is that the spin frustration does not occur, even though both signs of exchange interaction are incorporated.

As a prototype of this magnetism, we succeeded in manipulating Cr\textsuperscript{III} (t\textsubscript{3g} 2) are not changed but the ferromagnetic coupling between these metal ions is disconnected by irradiation. In the present work, we focus our attention on the optical-control of magnetic poles (N and S). In an optical magnetic memory media made of magnetic metals such as TbFe, the phenomenon of photothermally induced magnetic pole inversion is used. In this type of device, the magnetic material is heated above its Curie temperature (\(T\text{c}\)) by a photothermal process in the presence of a reverse external magnetic field, and then, during the cooling process below \(T\text{c}\), the magnetization occurs parallel to the external magnetic field, resulting in a magnetic pole inversion.\textsuperscript{(11)} In the present paper, we show a novel magnetic phenomenon “photoinduced magnetic pole inversion”. This phenomenon occurs even in the absence of an external magnetic field. Therefore, its mechanism is completely different from that of the photothermally induced magnetic pole inversion.

The present novel phenomenon can be achieved by a combination of the photoinduced change of magnetization\textsuperscript{(10)} and the mixed ferro-ferrimagnetism\textsuperscript{(12–16)} developed recently. In the latter magnetism, the weight average of the ferromagnetic and ferrimagnetic characters can be precisely controlled by fine-tuning of the composition. One of the most important characteristics for this magnet is that the spin frustration does not occur, even though both signs of exchange interaction are incorporated. As a prototype of this magnetism, we succeeded in manipulating

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both ferromagnetic ($J_{\text{NC}} > 0$) and antiferromagnetic ($J_{\text{NC}} < 0$) superexchange interactions independently with the compounds in the series of ($\text{Ni}^{II}\text{Mn}^{III}_{x}\text{Fe}^{III}_{1-x}$)$_{\text{y}}$[$\text{Cr}^{III}(\text{CN})_{6}$]$\cdot 7\text{H}_{2}\text{O}$ ($0 \leq x \leq 1$).12–14 Their magnetic properties such as the saturation magnetization ($M_s$), the coercive field ($H_c$), and the thermodynamics of magnetization including the compensation temperature ($T_{\text{comp}}$) could be controlled by fine-tuning the composition factor $x$, without spin glass behavior. In addition, in ($\text{Ni}^{II}\text{Mn}^{III}_{x}\text{Fe}^{III}_{1-x}$)$_{\text{y}}$[$\text{Cr}^{III}(\text{CN})_{6}$]$\cdot 7\text{H}_{2}\text{O}$ containing one antiferromagnetic interaction and two ferromagnetic interactions, we have recently succeeded in designing and synthesizing a novel magnet exhibiting two compensation temperatures, i.e., the spontaneous magnetization changes its sign twice with changing temperature.15

By a combination of this mixed ferro-ferrimagnetism and the photoinduced change of magnetization, we previously showed the first observation of photoinduced magnetic pole inversion using the ($\text{Fe}^{III}_{0.4}\text{Mn}^{III}_{0.6}$)$_{\text{y}}$[$\text{Cr}^{III}(\text{CN})_{6}$]$\cdot 7\text{H}_{2}\text{O}$ system.17 To understand this novel phenomenon, we show here (1) the details of the strategy and model calculations based on the MF theory, (2) the structures and magnetic properties of the members for the ($\text{Fe}^{III}_{0.4}\text{Mn}^{III}_{0.6}$)$_{\text{y}}$[$\text{Cr}^{III}(\text{CN})_{6}$]$\cdot 7\text{H}_{2}\text{O}$ system, (3) the optomagnetic behaviors of this system, and (4) the theoretical analysis of their observed photomagnetic phenomenon based on the MF theory.

II. Strategy

First, we show the strategy of the photoinduced magnetic pole inversion. The key of our strategy is to control the compensation temperature ($T_{\text{comp}}$) in a pure photon process. To meet this challenge, the theoretical prediction of the thermodynamics is indispensable. However, for classical metal or metal oxide magnets, such a prediction is difficult in general. One of the reasons is that various types of exchange and/or superexchange interactions exist among metals or metal ions. Moreover, the metal substitution often causes structural distortions. Conversely, for Prussian blue analogues,26–34 which are one of the most attractive classes of molecule-based magnets,35–38 the theoretical treatment becomes much simpler for the following reasons: (1) The face-centered cubic (fcc) structure of the Prussian blue analogues is maintained even when metal ion substitution is carried out. (2) Only the superexchange interactions between the nearest neighbor metal ions can operate among spin sources. In other words, contributions from the second nearest neighbor sites can be neglected due to the relatively long distances (10 Å) between those metal ions.12 Therefore, the design of novel magnets based on the simple MF theory is effective for Prussian blue analogues.

For ternary metal Prussian blue analogues, ($\text{A}^{II}_{1}\text{B}^{II}_{1-x-y}\text{B}^{III}$)$_{\text{y}}$[$\text{B}^{III}\text{Mn}^{II}(\text{CN})_{6}$], the thermodynamics of spontaneous magnetization can be evaluated, considering only two types of superexchange couplings between the nearest neighbor sites, one for A1-B and the other for A2-B (Figure 1). The molecular fields $H_{\text{A}1}$, $H_{\text{A}2}$, and $H_{\text{B}}$ acting on the three sublattice sites can be expressed as follows:

$$H_{\text{A}1} = H_0 + n_{\text{A}1}\mu_B M_B$$  

$$H_{\text{A}2} = H_0 + n_{\text{A}2}\mu_B M_B$$  

$$H_{\text{B}} = H_0 + n_{\text{BA}1}M_{\text{A}1} + n_{\text{BA}2}M_{\text{A}2}$$

Figure 1. Schematic diagram illustrating mixed ferro-ferrimagnetism with both ferromagnetic ($J_{\text{A}B} > 0$) and antiferromagnetic ($J_{\text{A}B} < 0$) interactions. The carbon (small gray) ends of the cyano groups are bonded to $\text{B}^{III}$ (black spheres), and the nitrogen (small white) ends are bonded to either A1$^{II}$ (white spheres) or A2$^{II}$ (gray spheres).
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\[ M_i = \lambda_i g \mu_B \langle S_i \rangle \]  

(5)

Substituting eqs 4 and 5 into eqs 1–3, we have

\[ H_{A1} = H_0 + \frac{2Z_{A1B} \langle J_{A1B} \rangle}{g \mu_B} \langle S_y \rangle \]  

(6)

\[ H_{A2} = H_0 + \frac{2Z_{A2B} \langle J_{A2B} \rangle}{g \mu_B} \langle S_y \rangle \]  

(7)

\[ H_B = H_0 + \frac{2Z_{B1A} \langle J_{A1B} \rangle}{g \mu_B} \langle S_A \rangle + \frac{2Z_{B2A} (1 - x) \langle J_{A2B} \rangle}{g \mu_B} \langle S_A \rangle \]  

(8)

The magnitudes of \( \langle S_i \rangle \), setting \( H_0 = 0 \), are given by

\[ \langle S_i \rangle = S_0 B_S \left( \frac{g \mu_B H_i S_i}{k_B T} \right) \]  

(9)

where \( B_S \) is the Brillouin function, \( S_0 \) is the value of \( \langle S_i \rangle \) at \( T = 0 \) K and \( k_B \) is the Boltzmann constant. The \( \langle S_i \rangle \) can be calculated numerically and then the sublattice magnetizations \( (M) \) in eq 5 are obtained. The total magnetization \( (M_{\text{total}}) \) can then be obtained by

\[ (M_{\text{total}}) = M_{A1} - M_{A2} + M_B \]  

(10)

Using this MF model, we can design the ternary metal Prussian blue analogues which exhibit negative magnetization, and predict their \( T_{\text{comp}} \) values.

For some Prussian blue analogues, we have shown that the spontaneous magnetization could be changed by photoirradiation. Therefore, by introducing such a photosensitive ferro (or ferrri) magnet to the mixed ferro-ferrimagnet, the thermodynamics of the magnetization would be controlled by photoirradiation. That is, if the photoinduced magnetization change proceeds at either the ferromagnetic or ferrimagnetic site in mixed ferro-ferrimagnets, the balance of magnetization between the ferromagnetic and ferrimagnetic site will change, resulting in the photoinduced magnetic pole inversion. Let us show a model calculation of this concept using spin crossover phenomenon. Here, we consider the \( (A1^{1-x}A2^{x})_{1.5}[B^{III}(CN)_{6}] \) magnet including a photosensitive site, in which the spin quantum numbers for the metal ions are \( S_{A1} = 1, S_{A2} = 2, \) and \( S_B = 3/2, \) and the \( J_{A1B} \) and \( J_{A2B} \) values are \( +5.0 \) and \( -2.5 \) cm\(^{-1}\). The temperature dependence of magnetization for \( x = 0.44 \) can be calculated using eqs 1–10 as shown in the upper curve (i) of Figure 2a. This curve is composed of the positive magnetizations derived from the \( A1 \) and \( B \) sublattices and the negative magnetization from the \( A2 \) sublattice. When the spin crossover occurs at the \( A1 \) metal ion of a ferromagnetic site by photoirradiation \( (S_{A1} = 1 \rightarrow S_{A1} = 0) \), the positive magnetization decreases and hence the magnetization reversal can occur as shown in the lower curve (ii) of Figure 2a. Similarly, the pole inversion can be expected, when the spin crossover occurs at the \( A2 \) metal ion of a ferrimagnetic site by photoirradiation \( (S_{A2} = 2 \rightarrow S_{A2} = 0) \). In this case, we consider the member for \( x = 0.36 \), which shows a compensation temperature before irradiation (Figure 2b, lower curve (i)). When the spin crossover proceeds from \( S_{A2} = 2 \) to \( S_{A2} = 0 \) at 20% of the \( A2 \) site, the magnetization curve changes to the upper curve (ii) in Figure 2b, showing the pole inversion at the temperature below \( T_{\text{comp}} \). We can thus design the magnet exhibiting the photoinduced magnetic pole inversion. Of course, this novel phenomenon will occur not only by photoinduced spin crossover but also by various types of photoinduced phenomenon such as photoinduced charge transfer among metal ions and photoinduced change of superexchange interaction.

As a prototype exemplifying our concept, we have designed a \( (Fe_{1.5}Mn_{0.36}Cr_{0.36})[Cr(CN)_{6}]\cdot7.5H_2O \) magnet containing both ferromagnetic (\( Fe \)) and antiferromagnetic (\( Mn \)) interactions. In this system, the magnetization of \( Fe_{1.5}[Cr(CN)_{6}]\cdot7.5H_2O \) for a ferromagnetic site is reduced by the visible light irradiation. Based on the Mössbauer experiments, we reported that this magnetization decrease is due to the photoinduced change of the \( J_{FeCr} \) value. Conversely, the \( Mn_{1.5}[Cr(CN)_{6}]\cdot7.5H_2O \) for a ferrimagnetic site has no absorption in the visible region and hence does not change the magnetization by visible light irradiation. Using this mixed ferro-ferrimagnet, we demonstrate the photoinduced magnetic pole inversion.

**III. Experimental Section**

A. Synthesis. For the preparation of the Prussian blue analogues incorporating three different metal ions, \( (Fe^{II},Mn^{II},Cr^{III})[Cr(CN)_{6}]\cdot7.5H_2O \), a 50 cm\(^3\) aqueous solution (0.02 mol dm\(^{-3}\)) containing \( FeCl_3 \) and \( MnCl_2 \) was added to a concentrated aqueous solution (7 cm\(^3\)) of \( K_3[Cr(CN)_{6}] \) (0.1 mol dm\(^{-3}\)), yielding a light brown colored microcrystalline powder. The precipitate was dialyzed for 48 h and then filtered. The fraction \( (x_{\text{max}}) \) of \( Fe^{II} \) vs \( (Fe^{II} + Mn^{II}) \) in the above diluted aqueous solution was varied from 0 to 1, keeping the total metal ion concentration at 0.02 mol dm\(^{-3}\). Elemental analyses for C, H, and N were carried out.
by standard microanalytical methods. Those for Mn, Fe, and Cr were analyzed by atomic absorption spectrometry.

B. Measurements. FT-IR spectra were recorded on a Biorad Model FTS 40 A spectrometer. X-ray powder diffraction was measured on a Rigaku PW 1370 powder diffractometer. Magnetic susceptibility and magnetization measurements were carried out using a Quantum Design MPMS 7 superconducting quantum interference device (SQUID) magnetometer. A sample (∼50 μg) supported on a commercial transparent adhesive tape was placed on the edge of an optical fiber. A weak blue light (360–450 nm, 2 mW/cm²) of a Xe lamp was guided via an optical fiber into the SQUID magnetometer as an exciting light source.

IV. Results and Discussion

A. Structures. The elemental analyses for the synthesized complexes showed that the experimentally obtained x values were slightly larger than the x_{max} values used in the syntheses, e.g., x = 0.18 (x_{max} = 0.10), 0.60 (x_{max} = 0.50), and 0.92 (x_{max} = 0.90). The CN stretching frequencies in the IR spectra for complexes showed that the experimentally obtained

Figure 3. Calculated and experimentally observed saturation magnetizations for (Fe^{II},Mn^{II}_{1-x})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O as a function of x: calculated (−) and observed (○).

and Fe II are randomly incorporated at nitrogen sites in the lattice.

B. Magnetic Properties. (a) Saturation Magnetization. The saturation magnetizations for Fe^{II}_{1-x}[Cr^{III}(CN)_{6}]·H_{2}O (x = 1)

39) Analyses: Calcd for Mn, Cr, H, O: Mn, 19.36; Cr, 12.22; C, 16.93; N, 19.75; H, 5.17. Found: Mn, 19.13; Cr, 12.53; C, 16.68; N, 19.42; H, 30.57. Calcd for (Fe_{0.9},Mn_{0.1})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 3.73; Mn, 16.99; Cr, 13.04. Found: Fe, 3.77; Mn, 17.19; Cr, 12.72. Calcd for (Fe_{0.9},Mn_{0.1})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 6.18; Mn, 12.10; Cr, 11.48. Found: Fe, 6.15; Mn, 12.04; Cr, 11.12. Calcd for (Fe_{0.92},Mn_{0.08})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 7.94; Mn, 11.5; Cr, 12.2; C, 16.9; N, 19.7. Found: Fe, 8.03; Mn, 11.5; Cr, 11.9; C, 17.1; N, 19.7. Calcd for (Fe_{0.92},Mn_{0.08})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 7.90; Mn, 11.67; Cr, 12.74. Found: Fe, 7.88; Mn, 11.74; Cr, 12.97. Calcd for (Fe_{0.92},Mn_{0.08})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 10.15; Mn, 8.56 Cr, 11.70. Found: Fe, 10.17; Mn, 8.58; Cr, 12.45. Calcd for (Fe_{0.6},Mn_{0.4})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 12.32; Mn, 8.06; Cr, 12.73. Found: Fe, 12.28; Mn, 8.03; Cr, 12.65. Calcd for (Fe_{0.6},Mn_{0.4})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 14.08; Mn, 6.32 Cr, 12.73. Found: Fe, 14.19; Mn, 6.37; Cr, 13.10. Calcd for (Fe_{0.6},Mn_{0.4})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 15.28; Mn, 4.70; Cr, 12.45. Found: Fe, 15.35; Mn, 4.72; Cr, 13.06. Calcd for (Fe_{0.6},Mn_{0.4})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 17.09; Mn, 2.92; Cr, 12.43. Found: Fe, 17.12; Mn, 2.92; Cr, 13.02. Calcd for (Fe_{0.6},Mn_{0.4})_{1.5}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 17.70; Mn, 1.49; Cr, 11.93. Found: Fe, 17.87; Mn, 1.51; Cr, 12.54. Calcd for Fe_{x}[Cr^{III}(CN)_{6}]·H_{2}O: Fe, 19.62; Cr, 12.18; C, 16.88; N, 19.69; H, 3.5. Found: Fe, 19.6; Cr, 12.4; C, 16.9; N, 20.2; H, 3.2.

and Fe^{II}_{1.5}[Cr^{III}(CN)_{6}]·7.5H_{2}O (x = 0) were 6.6 and 4.4 μB respectively. The M_{s} values for the Fe^{II}_{1.5}[Mn^{II}_{1-x}][Cr^{III}(CN)_{6}]·7.5H_{2}O series showed a systematic change as a function of x. As seen in Figure 3, the observed M_{s} values for 0 < x < 0.4 decreased linearly with increasing x. In contrast, above x = 0.4, the M_{s} values increased linearly with increasing x. The minimum M_{s} value, at x close to 0.4, was nearly zero. For the ternary metal Prussian blue analogues, parallel spins and antiparallel spins can partially or even completely cancel, depending on x. Therefore, using the spin quantum numbers for the metals (Fe^{II} = 2, Mn^{II} = 5/2, Cr^{III} = 3/2), together with x, the theoretical M_{s} values for the members of the series (Fe^{II}_{1-x}[Mn^{II}_{1-x}][Cr^{III}(CN)_{6}] can be calculated by eq 11,12 assuming the g factor of 2.

\[
M_s = 2[S_C + 1.5[S_Fe - S_{Mn}(1 - x)]]
\]

The calculated x dependence of the M_{s} value was similar to the observed one, indicating that these magnets were obtained without spin glass behavior and their magnetic properties are explained by the MF model described in section II. However, the experimental composition for the minimum M_{s} value was slightly different from the calculated one. One of the reasons is that the observed M_{s} value of 6.6 μB for Fe^{II}_{1.5}[Cr^{III}(CN)_{6}] is smaller than the theoretical M_{s} value of 9.0 μB.

(b) Curie Temperature. The T_{c} values of this series decreased monotonically from 67 to 21 K with increasing x, as shown in Figure 4. For binary metal Prussian blue analogues, A_{i}[B(CN)_{6}], their theoretical T_{c} values are given by

\[
T_c = \sqrt{\frac{C_A C_B B_{BA}}{2}}
\]

where C_{i} (i = A, B) are Curie constants; C_{i} = \lambda N g^2 μ_s^2 S(S_i + 1)/\beta k.12 Conversely, the theoretical T_{c} value for the present ternary metal Prussian blue analogues is expressed as follows:

\[
T_c = \sqrt{\frac{C_{Fe} C_{Cr} n_{FeCr}}{2} + C_{Mn} C_{Cr} n_{MnCr}}
\]

= \sqrt{1.5S_{Cr} (S_{Cr} + 1)(xS_{Fe} + 1)n_{FeCr} - 1 + (1 - x)S_{Mn} (S_{Mn} + 1)n_{MnCr} - 1)}

This equation shows that T_{c} varies as a function of a weighted average of molecular fields (\lambda n_{FeCr} and n_{MnCr}), and thus suggests that T_{c} changes continuously from the T_{c} value of Mn^{II}_{1.5}[Cr^{III} (CN)_{6}] to that of Fe^{II}_{1.5}[Cr^{III}(CN)_{6}] with increasing x.

(c) Compensation Temperature. Figure 5 shows the magnetization vs temperature curves at 10 G with various x values. The present materials exhibited various types of thermodynamics
of magnetization, depending on $x$. Particularly, the materials where $x$ was 0.40–0.42 exhibited negative magnetization below $T_{\text{comp}}$. These various types of temperature dependence of the magnetization and compensation temperatures could be understood based on the MF model, by considering only the superexchange interactions between the nearest neighbors (Fe$^{III}$–Cr$^{III}$ and Mn$^{II}$–Cr$^{III}$). These magnetic phenomena arise because the positive magnetization due to the Mn$^{II}$ sublattice and the negative magnetizations due to the Fe$^{III}$ and Cr$^{III}$ sublattices have different temperature dependences. As an example, Figure 6 shows the calculated thermodynamics of sublattice and total magnetizations for $x = 0.40$. For this composition, the relations of the magnitude among the sublattice magnetizations are expressed as follows: $|M_{Fe} + M_{Cr}| < |M_{Mn}|$ at $T > T_{\text{comp}}$ and $|M_{Fe} + M_{Cr}| > |M_{Mn}|$ at $T < T_{\text{comp}}$.

(d) **Coercive Field.** The coercive field ($H_c$) is a significant parameter for the present work because negative magnetization below $T_{\text{comp}}$ must be maintained under external magnetic field.

Fortunately, the $H_c$ values for the magnets exhibiting compensation temperatures were much larger than an applied external magnetic field of 10 G (Figure 7). Especially, $H_c$ values for the magnets where $x$ was close to 0.4 were much larger than those at other $x$ values, e.g., 6 ($x = 0$), 2200 ($x = 0.42$), and 200 G ($x = 1$). In general, the $H_c$ value depends on the grain size of the sample. However, if the grain sizes are nearly the same, the $H_c$ values are expected to be proportional to the $M_{s}^{-1}$ values. This relation was observed with the series of (Ni$^{II}_{x}$Mn$^{II}_{1-x}$)$_{1.5}$[Cr$^{III}$,(CN)$_6$]$_7.5$H$_2$O. The same holds true for the series of the present (Fe$^{II}_{x}$Cr$^{III}_{1-x}$)$_{1.5}$[Cr$^{III}$,(CN)$_6$]$_7.5$H$_2$O system.

C. **Photoinduced Magnetic Pole Inversion.** We demonstrate the photoinduced magnetic pole inversion using the (Fe$^{II}_{1-x}$Mn$^{II}_{x}$)$_{1.5}$[Cr$^{III}$,(CN)$_6$]$_7.5$H$_2$O system. Let us first show the photomagnetic effect of the elemental compounds, Fe$_{1.5}$[Cr$^{III}$,(CN)$_6$]$_7.5$H$_2$O ($x = 1$) ferromagnet and Mn$_{1.5}$[Cr$^{III}$,(CN)$_6$]$_7.5$H$_2$O ($x = 0$) ferrimagnet. A visible light-induced magnetization decrease occurred with Fe$_{1.5}$[Cr$^{III}$,(CN)$_6$]$_7.5$H$_2$O. By irradiation with a filtered blue light (360–450 nm, 2 mW cm$^{-2}$) at 5 K, for example, ca. 10% of magnetization was decreased for 8 h of irradiation at 10 G (Figure 8). This reduced magnetization persisted for a period of several days at 5 K after turning off the light. The magnetic property of this irradiated sample returned to the initial one when the temperature of the sample was raised above 40 K, showing that the magnetization can be reduced by a photon mode and recovered by a thermal mode repeatedly. According to the Mössbauer experiments, the spin state of Fe$_{1.5}$[Cr$^{III}$,(CN)$_6$]$7.5$H$_2$O is not changed by the photoirradiation. Therefore, this photoinduced magnetization decrease will be due to the change of the superexchange interaction between Fe$^{III}$ and Cr$^{III}$. Thephotoexcited state is the mixed valence state of Cr$^{III}$–CN–Fe$^{III}$ and Fe$^{III}$–CN–Fe$^{III}$, which relax to a metastable state immediately where the ferromagnetic interaction is too weak to maintain the spin ordering. This metastable state returns to the original ferromagnetic state above 40 K. Conversely, the Mn$_{1.5}$[Cr(CN)$_6$]$7.5$H$_2$O for a ferrimagnetic site has no absorption in the visible region and hence did not show any change of magnetization by the visible light irradiation.

(40) The observed magnetization values were smaller than the calculated ones. This is because the calculated spontaneous magnetizations are essentially the saturated values, as the MF theory does not consider the magnetization process. In the experiment, however, the observed magnetization depends on the external magnetic field and the values obtained in the present experiment are not saturated ones.

To demonstrate the photoinduced magnetic pole inversion phenomenon, we chose (Fe$^{II}$,Mn$^{II}$)$_{1.5}$[Cr$^{III}$ (CN)$_6$]·7.5$\text{H}_2\text{O}$, which exhibits a negative magnetization ($T_{\text{comp}} = 19\text{ K}$). When this sample was irradiated at 16 K with the filtered blue light (360–450 nm), the negative magnetization at 16 K gradually became positive under an existing external field of 10 G (Figure 9a). Simultaneously, the $T_{\text{comp}}$ value shifted to a smaller value (19 K $\rightarrow$ 13 K $\rightarrow$ 7 K) and finally disappeared as shown in Figure 9b. This inverted magnetic pole persisted for a period of several days at 16 K after turning off the light. The magnetic pole inversion phenomenon is a photoinduced effect and not due to the heating of the sample under illumination. This is because, in the dark, the magnetization under 10 G did not vary at all by a slight change of the temperature; e.g. 16 K $\rightarrow$ 20 K $\rightarrow$ 16 K. The present novel phenomenon can be reasonably explained by the fact that the ratio of the ferromagnetic part (Fe$^{II}$–Cr site) to the ferrimagnetic part (Mn$^{II}$–Cr site) of magnetization changed due to the decrease of magnetization in the ferrimagnetic sites. Moreover, the magnetization vs temperature curve was recovered by warming to 80 K. The magnetic pole inversion thus can be induced repeatedly by alternate optical and thermal stimulations.

To proceed, the photoinduced magnetic pole inversion under the present experimental condition needs a rather long time irradiation. One of the main reasons could be a very low quantum yield of the photoreaction. Another reason comes from the weak light intensity (2 mW/cm$^2$) used here to avoid raising the temperature of the sample during the measurement in the SQUID. By increasing the light intensity, the reaction rate can be increased. Especially when a pulsed laser is used as the light source, the rate may increase drastically because the present experimental condition needs a rather long time of several days at 16 K after turning off the light. The magnetic pole inversion thus can be induced repeatedly by alternate optical and thermal stimulations.

D. Simulation with MF Theory. The present photoinduced magnetic pole inversion can be simulated by using the MF model. First we analyze the photoinduced magnetization decrease of Fe$_{1.5}$[Cr(CN)$_6$]·7.5$\text{H}_2\text{O}$. From the results of $^{57}$Fe Mössbauer measurements, we know that the spin state of Fe$^{II}$ does not change by irradiation and that neither electron transfer nor spin transition occur photochemically, but the ferromagnetic coupling of Fe$^{II}$ and Cr$^{III}$ is disconnected by irradiation. In other words, the ferromagnetic Fe$^{II}$ metal ions were changed to paramagnetic ions by photoirradiation. Therefore, we assume that the ferromagnetic coupling between the Fe$^{II}$ ion and the surrounding Cr$^{III}$ ions is disconnected. Then the molecular fields $H_{\text{Fe}}$, $H_{\text{Fe}}'$, and $H_{\text{Cr}}$ acting on the sublattice sites after irradiation can be expressed as follows:

$$H_{\text{Fe}} = H_0 + n_{\text{FeCr}}M_{\text{Cr}}$$

$$H_{\text{Fe}}' = H_0 + n_{\text{FeCr}}'M_{\text{Cr}}$$

$$H_{\text{Cr}} = H_0 + n_{\text{CrFe}}M_{\text{Fe}} + n_{\text{CrFe}}'M_{\text{Fe}}$$

where the $n_j$ and $n'_j$ are the molecular field coefficients of nonconverted and photoconverted sites, respectively, relating to the exchange coefficients ($J_j$ and $J'_j$). The $J_{\text{FeCr}}$ value of 0.9 cm$^{-1}$ before irradiation can be obtained from the experimental $^{57}$Fe Mössbauer measurements, we know that the spin state of Fe$^{II}$ does not change by irradiation and that neither electron transfer nor spin transition occur photochemically, but the ferromagnetic
**Figure 10.** Simulation of the photoinduced magnetization decrease for Fe$^{II}_{0.40}$Mn$^{II}_{0.60}$]$_{1.5}$[Cr$^{III}$(CN)$_6$]$_2$H$_2$O based on the MF theory. Upper and lower curves are the calculated temperature dependences of magnetization before and after the irradiation, respectively, based on eqs 14–16.

$T_c$ value of 21 K, and the $J_{FeCr'}$ value is assumed to be zero. We also have to take into consideration a spatial distribution of the photoconverted site, because the concentration of the disconnected sites may be lower at deeper sites from the surface of the photoconverted site, because the concentration of the $c$ value of 21 K, and the $J_{FeCr}$ value is assumed to be zero.

We next simulate the photoinduced magnetization reversal of the material for $x = 0.40$, by a combination of theoretical treatment for the photoinduced change of magnetization and that for ternary metal Prussian blue analogues. The molecular fields $H_{Fe}$, $H_{Cr'}$, $H_{Mn}$, and $H_{Cr}$ acting on each sublattice site in $(Fe,Mn_{1−x})_{1.5}[Cr(CN)_{6}]•2H_{2}O$ can be expressed as follows:

$$H_{Mn} = H_0 + n_{MnCr}M_{Cr} \quad (17)$$

$$H_{Fe} = H_0 + n_{FeCr}M_{Cr} \quad (18)$$

$$H_{Fe'} = H_0 + n_{FeCr'}M_{Cr} \quad (19)$$

$$H_{Cr} = H_0 + n_{CrMn}M_{Mn} + n_{CrFe}M_{Fe} + n_{CrFe'}M_{Fe'} \quad (20)$$

The $J_{MnCr}$ value of $−2.5 \text{cm}^{-1}$ is obtained from the experimental critical temperature of Mn$^{II}_{1.4}[Cr^{III}$(CN)$_6]$•7.5H$_2$O ($T_c = 67 \text{K}$). Under these conditions, the temperature dependence of the total magnetization of $(Fe^{II}_{0.40}Mn^{II}_{0.60})_{1.5}[Cr^{III}$(CN)$_6]$•7.5H$_2$O before irradiation was calculated as shown in Figure 11. This calculated curve is consistent with the experimental curve qualitatively, although its $T_{comp}$ value is slightly larger. Then, the magnetization vs temperature curve after irradiation was evaluated under similar conditions to the photoinduced magnetization decrease of Fe$^{II}_{1.5}$Cr$^{III}$(CN)$_6$•7.5H$_2$O. The calculated curve agreed with the experimentally obtained curve qualitatively. This correspondence shows that the present magnetic pole inversion is obtained according to our strategy. That is, the photoinduced magnetization change proceeds at the ferromagnetic site in the mixed ferro-ferrimagnet, and the balance of magnetization between the ferromagnetic and ferrimagnetic site changes, resulting in the photoinduced magnetic pole inversion.

**V. Conclusion**

We have demonstrated the photoinduced magnetic pole inversion in a ferro-ferrimagnet $(Fe^{II}_{x}Mn^{II}_{1−x})_{1.5}[Cr^{III}$(CN)$_6]$•7.5H$_2$O, by a combination of mixed ferro-ferrimagnetism and photomagnetism. Although the mechanism of the photoinduced process is not very clear, we can purpose the design of the novel magnets based on the MF theory. The present phenomenon occurs only at very low temperature ($<19 \text{K}$). This is due to the low $T_c$ value of the molecule-based magnets used here. However, by designing the spin sources and the structure of compounds, the $T_c$ value of Prussian blue analogues increases gradually. For example, very recently, Girolami et al. and Miller et al. have succeeded in preparing K$^{IV}_{x}[Cr^{III}$(CN)$_6]$ with $T_c = 103 \text{K}$ and $K^{IV}_{x=0.59}[Cr^{III}$(CN)$_6]$•0.79(SO$_4$)$_{0.08}$•0.93H$_2$O with $T_c = 99 \text{K}$, respectively. We have also succeeded in obtaining K$^{IV}_{x=0.4}[Cr^{III}$(CN)$_6$]•0.87•7.0H$_2$O•0.4C$_2$H$_5$OH film ($T_c = 72 \text{K}$) by using the electrochemical method. We thus believe that a room-temperature photoinduced magnetic pole inversion is possible in the future, by applying the present strategy to those high $T_c$ molecule-based magnets.

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