Design and Preparation of a Novel Magnet Exhibiting Two Compensation Temperatures Based on Molecular Field Theory

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We show the design and preparation of a novel type of magnet exhibiting *two compensation temperatures;* i.e., the spontaneous magnetization changes its sign twice with changing temperature. The key to obtaining this unusual behavior is the simultaneous incorporation of one antiferromagnetic and two different ferromagnetic interactions through the use of four different spin sources, as predicted by a calculation based on molecular field theory. As a prototype exemplifying this idea, we have prepared a Prussian blue analog, $(\mathrm{Ni}^{\mathrm{II}}_{0.22}\mathrm{Mn}^{\mathrm{II}}_{0.60}\mathrm{Fe}^{\mathrm{II}}_{0.18})_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 7.6\mathrm{H_2O}$, which exhibits magnetization reversals at 35 and 53 K. [S0031-9007(98)08379-3]

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Control of magnetic properties is one of the most attractive but also most difficult targets in the field of magnetic materials. Particularly, the control of the thermodynamics of magnetization is very difficult. Most magnetic materials exhibit monotonic increases in magnetization with decreasing temperature below their critical temperatures (T_c). However, in the classical theory of ferrimagnets, Néel had envisaged the possibility that the spontaneous magnetization can change sign; i.e., the magnetic poles can invert, at a particular temperature (the so-called compensation temperature, T_{comp}) [1]. In fact, magnetic materials such as $\mathrm{NiFe}_{2-x}\mathrm{V}_x\mathrm{O}_4$ and $\mathrm{NBu}_4[\mathrm{Fe}^{\mathrm{II}}\mathrm{Fe}^{\mathrm{III}}(\mathrm{C_2O_4})_3]$, exhibiting negative magnetization, have been found [2–7].

The objective in the present work is the design and preparation of novel types of magnets exhibiting *two compensation temperatures,* i.e., a zero-field magnetization curve that passes through zero twice before finally reaching the paramagnetic phase. In order to meet this challenge, the theoretical prediction of the magnetic properties is an absolute requirement. However, for classical metal or metal oxide magnets, such a prediction is difficult in general. One of the main reasons is that various types of exchange and/or superexchange interactions exist among many spin sources. Moreover, the metal or metal ion substitution often causes structural distortions. Conversely, for Prussian blue analogs [8–16], some of which, e.g., $\mathrm{CsNi}[\mathrm{Cr(CN)}_6]$, become ferromagnets below 90 K [12], and others, such as $\mathrm{V}_{1.16}[\mathrm{Cr(CN)}_6]$, which are ferrimagnets below 315 K [13], the theoretical treatment is much simpler for the following reasons. (1) Only the superexchange interactions between the nearest neighbor metal ions have to be considered. In other words, contributions from the second nearest neighbor sites can be neglected due to the relatively long distances between metal ions [17]. (2) The character of superexchange interactions can be easily predicted from a simple orbital symmetry rule, because the directions of the symmetry axes of the spin source d orbitals for all of the metal ion sites and all of the ligand p orbitals are identical due to their face-centered-cubic (fcc) structure [11]. Therefore, the design of novel magnets based on molecular field (MF) theory is effective for the class of Prussian blue analogs. In fact, using ternary metal Prussian blue analogs incorporating both ferromagnetic and antiferromagnetic exchange interactions simultaneously [17–20], we have succeeded in tuning their T_{comp} values based on MF theory and the use of three sublattice sites [17].

The key objective of the present study was to design Prussian blue analogs containing both ferromagnetic and antiferromagnetic interactions simultaneously by incorporating *four* different metal ions in the lattice, three being randomly distributed, with the correct ratio being obtained by the use of a calculation based on MF theory. As a prototype exemplifying our idea, we have prepared members of a new class of mixed ferroferrimagnets with the generic formula $(\mathrm{Ni}^{\mathrm{II}}_a\mathrm{Mn}^{\mathrm{II}}_b\mathrm{Fe}^{\mathrm{II}}_c)_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot z\mathrm{H_2O}$ ($a + b + c = 1$). Among these compounds, that with the composition $a = 0.22, b = 0.60, c = 0.18$ showed two compensation temperatures ($T_{\mathrm{comp\,1}} = 53$ K and $T_{\mathrm{comp\,2}} = 35$ K). To our knowledge, this is the first magnet exhibiting *two compensation temperatures* [21].

First, we theoretically evaluated the temperature dependences of a series of compounds $(\mathrm{Ni}^{\mathrm{II}}_a\mathrm{Mn}^{\mathrm{II}}_b\mathrm{Fe}^{\mathrm{II}}_c)_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot z\mathrm{H_2O}$ using MF theory, with the spin numbers for the four sublattice sites: $S_{\mathrm{Ni}} = 1$, $S_{\mathrm{Mn}} = 5/2$, $S_{\mathrm{Fe}} = 2$, and $S_{\mathrm{Cr}} = 3/2$ (Fig. 1). For this calculation, only the three types of superexchange couplings between the nearest neighbor sites, Ni-Cr, Mn-Cr, and Fe-Cr, were considered. The molecular fields H_{Ni}, H_{Mn}, H_{Fe}, and H_{Cr} acting on the four sublattice sites

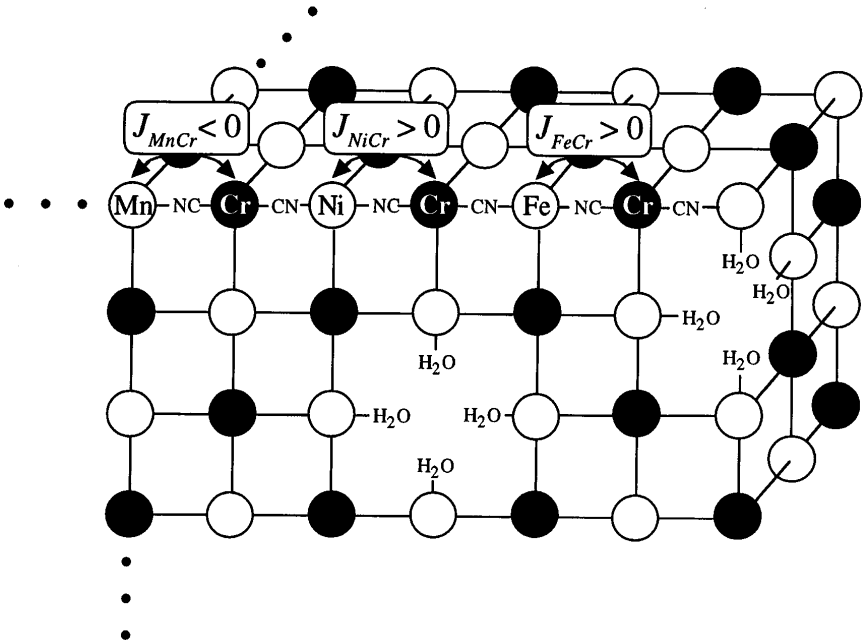

FIG. 1. Schematic illustration of mixed ferroferrimagnets composed of $(\mathrm{Ni}_a^{\mathrm{II}}\mathrm{Mn}_b^{\mathrm{II}}\mathrm{Fe}_c^{\mathrm{II}})_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot z\mathrm{H_2O}$. Zeolitic water molecules in the unit cell are omitted for clarity. The ferromagnetic ($J_{\mathrm{NiCr}} > 0$ and $J_{\mathrm{FeCr}} > 0$) and antiferromagnetic ($J_{\mathrm{MnCr}} < 0$) superexchange interactions can coexist without spin frustration, because the A^{II} (A = Ni, Mn, or Fe) (○) and $\mathrm{Cr}^{\mathrm{III}}$ (●) ions of the Prussian blue structure are linked in an alternating fashion.

can be expressed as follows:

$$\begin{aligned} H_{\mathrm{Mn}} &= H_0 + n_{\mathrm{MnCr}} M_{\mathrm{Cr}}\,, \\ H_{\mathrm{Ni}} &= H_0 + n_{\mathrm{NiCr}} M_{\mathrm{Cr}}\,, \\ H_{\mathrm{Fe}} &= H_0 + n_{\mathrm{FeCr}} M_{\mathrm{Cr}}\,, \\ H_{\mathrm{Cr}} &= H_0 + n_{\mathrm{CrMn}} M_{\mathrm{Mn}} + n_{\mathrm{CrNi}} M_{\mathrm{Ni}} + n_{\mathrm{CrFe}} M_{\mathrm{Fe}}\,, \end{aligned} \tag{1}$$

where H_0 is the external magnetic field, the various n_{ij} are the molecular field coefficients relating to the exchange coefficients (J_{ij}), and M_{Ni}, M_{Mn}, M_{Fe}, and M_{Cr} are sublattice magnetizations per unit volume for the respective metal sites. The sublattice magnetizations and total magnetization ($M_{\mathrm{total}} = -M_{\mathrm{Mn}} + M_{\mathrm{Ni}} + M_{\mathrm{Fe}} + M_{\mathrm{Cr}}$) as a function of temperature can be evaluated using a Brillouin function. A J_{MnCr} value of $-2.5\ \mathrm{cm}^{-1}$, a J_{NiCr} value of $+5.6\ \mathrm{cm}^{-1}$, and a J_{FeCr} value of $+0.9\ \mathrm{cm}^{-1}$ were obtained from the experimental T_c values of $\mathrm{Mn}_{1.5}^{\mathrm{II}}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 7.5\mathrm{H_2O}$ ($T_c = 67$ K) [17], $\mathrm{Ni}_{1.5}^{\mathrm{II}}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 8\mathrm{H_2O}$ ($T_c = 72$ K) [17], and $\mathrm{Fe}_{1.5}^{\mathrm{II}}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 7.5\mathrm{H_2O}$ ($T_c = 21$ K) [19], respectively. Using these J values and the compositional factors (a, b, c), the temperature dependences were theoretically evaluated. Figure 2 shows the calculated temperature dependence curves for each sublattice $(M_{\mathrm{Mn}}, M_{\mathrm{Ni}}, M_{\mathrm{Fe}}, M_{\mathrm{Cr}})$ and the total magnetization (M_{total}) for the $(\mathrm{Ni}_{0.20}^{\mathrm{II}}\mathrm{Mn}_{0.61}^{\mathrm{II}}\mathrm{Fe}_{0.19}^{\mathrm{II}})_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot z\mathrm{H_2O}$ system, which exhibits two compensation temperatures. On the basis of this theoretical prediction, we synthesized members of this series.

The compounds were prepared by reacting mixtures of $\mathrm{NiCl_2}$, $\mathrm{MnCl_2}$, and $\mathrm{FeCl_2}$ aqueous solutions with $\mathrm{K_3Cr(CN)_6}$ aqueous solution to yield light brown precipitates. The precipitates were dialyzed for 48 h and then filtered. Elemental analyses for Mn, Ni, Fe, and Cr were obtained by inductively coupled plasma-atomic emission spectrometry, and those for C, H, and N were carried out by standard microanalytical methods, e.g., calculated for $(\mathrm{Ni}_{0.22}^{\mathrm{II}}\mathrm{Mn}_{0.60}^{\mathrm{II}}\mathrm{Fe}_{0.18}^{\mathrm{II}})_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 7.6\mathrm{H_2O}$: Ni, 4.6; Mn, 11.5; Fe, 3.4; Cr, 12.1; C, 16.8; N, 19.6; H, 3.6, and found Ni, 4.6; Mn, 11.5; Fe, 3.4; Cr, 12.6; C, 16.8; N, 19.4; H, 3.4. The CN stretching frequency in the IR spectra for the resulting complexes changed continuously depending on the mixing ratio. The x-ray powder diffraction patterns for these compounds confirmed the fcc structure. The lattice constants varied continuously depending on the composition. By analogy with the ternary metal Prussian blue analogs, these results indicate that $\mathrm{Ni}^{\mathrm{II}}$, $\mathrm{Mn}^{\mathrm{II}}$, and $\mathrm{Fe}^{\mathrm{II}}$ are randomly incorporated in sites where they are coordinated to the nitrogen ends of the cyano groups, and the $\mathrm{Cr}^{\mathrm{III}}$ ions are always coordinated to the carbon ends of the cyano groups.

Magnetization measurements for these compounds were carried out using a Quantum Design MPMS 5 superconducting quantum interference device magnetometer. Figure 3 shows the field-cooled magnetization vs temperature plots for the $(\mathrm{Ni}_{0.22}^{\mathrm{II}}\mathrm{Mn}_{0.60}^{\mathrm{II}}\mathrm{Fe}_{0.18}^{\mathrm{II}})_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 7.6\mathrm{H_2O}$ powder in an external magnetic field of 10 G. This compound showed two compensation temperatures ($T_{\mathrm{comp\,1}} = 53$ K and $T_{\mathrm{comp\,2}} = 35$ K). Its remanent

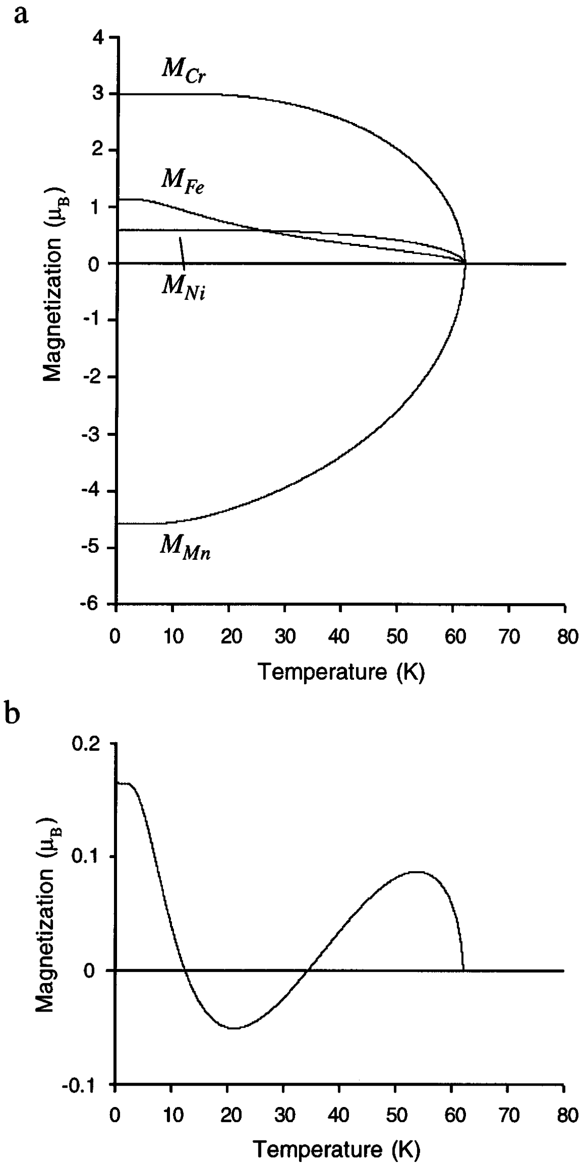

FIG. 2. Calculated temperature dependence curves for each sublattice and total magnetization for $(\mathrm{Ni}^{\mathrm{II}}_{0.20}\mathrm{Mn}^{\mathrm{II}}_{0.61}\mathrm{Fe}^{\mathrm{II}}_{0.19})_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot z\mathrm{H_2O}$, based on molecular field theory, with four sublattice sites (Ni, Mn, Fe, Cr), with J coefficients $J_{\mathrm{NiCr}} = +5.6\ \mathrm{cm}^{-1}$, $J_{\mathrm{FeCr}} = +0.9\ \mathrm{cm}^{-1}$, and $J_{\mathrm{MnCr}} = -2.5\ \mathrm{cm}^{-1}$: (a) sublattice magnetization (M_{Mn}, M_{Ni}, M_{Fe}, M_{Cr}); and (b) total magnetization (M_{total})

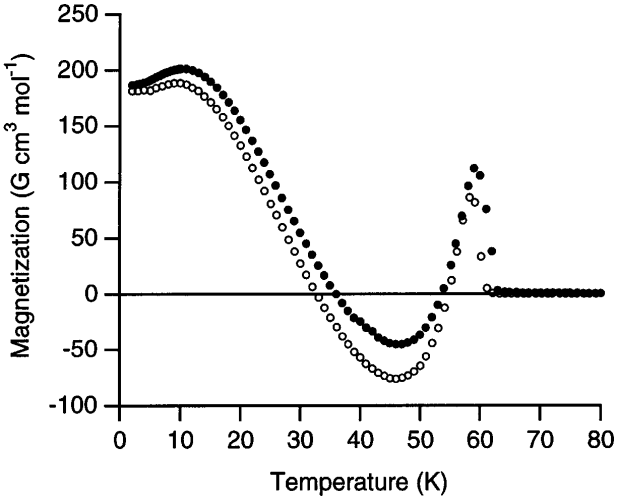

FIG. 3. Experimental magnetization vs temperature curves for $(\mathrm{Ni}^{\mathrm{II}}_{0.22}\mathrm{Mn}^{\mathrm{II}}_{0.60}\mathrm{Fe}^{\mathrm{II}}_{0.18})_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 7.6\mathrm{H_2O}$: (●) field-cooled magnetization obtained with decreasing temperature (80 K ⟶ 2 K) in an external magnetic field of 10 G; (○) remanent magnetization obtained with increasing temperature (2 K ⟶ 80 K) after the temperature was first lowered in the applied magnetic field of 10 G.

magnetization vs temperature plots also showed a similar behavior. The theoretical calculation described above shows clearly that the two compensation temperatures for this compound are due to different temperature dependences of the negative magnetization of the $\mathrm{Mn^{II}}$ sublattice and the positive magnetization of the $\mathrm{Ni^{II}}$, $\mathrm{Fe^{II}}$, and $\mathrm{Cr^{III}}$ sublattices. In the temperature range between 61 K (T_c) and 53 K, the positive magnetizations dominate. Between 53 and 35 K, however, the negative magnetization outweighs the positive magnetizations. At temperatures below 35 K, the positive magnetizations again dominate due to the growth of the $\mathrm{Fe^{II}}$ sublattice contribution. Other magnetic properties also obeyed the theory of mixed ferroferrimagnetism [17]. For example, the saturation magnetization (I_s) value for the composition $a = 0.24$, $b = 0.58$, $c = 01.8$ was $0.77\mu_B$, assuming the g factors for the metal ions to be 2.0. This observed value is close to the theoretical I_s value of $0.52\mu_B$ [22]. In addition, the coercive field (H_c) value of 570 G was larger than the H_c values for the respective binary compositions $\mathrm{Mn}^{\mathrm{II}}_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 7.5\mathrm{H_2O}$ ($H_c = 6$ G), $\mathrm{Ni}^{\mathrm{II}}_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 8\mathrm{H_2O}$ ($H_c = 120$ G) and $\mathrm{Fe}^{\mathrm{II}}_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6] \cdot 7.5\mathrm{H_2O}$ ($H_c = 200$ G). This is because the H_c values for the mixed ferroferrimagnets are proportional to $(I_s)^{-1}$ [17].

In summary, we have succeeded in designing and synthesizing a novel type of magnet exhibiting a double magnetic pole inversion with changing temperature. One of the main reasons for the success of this approach is that the fcc structure of the Prussian blue analogs is maintained even when the metal ions are substituted. Another reason is that spin frustration does not occur in this system, because the A^{II} ($\mathrm{Ni^{II}}$, $\mathrm{Mn^{II}}$, and $\mathrm{Fe^{II}}$) and $\mathrm{Cr^{III}}$ ions are linked in an alternating fashion. Prussian blue analogs, which are prime examples of molecule-based magnets [23–26], are useful for the molecular design of mixed ferroferrimagnets, because various types of metal ions can be easily incorporated as spin centers. To date, we have succeeded in demonstrating several new phenomena such as the photoinduced increase of magnetization [27], the photoinduced magnetic pole inversion [19], and the tuning of the color of magnetic thin films [20]. Moreover, we have recently obtained a high-T_c (340 K) transparent magnetic film, composed of vanadium chromium polycyanide, which exhibits a Faraday effect at room temperature [28]. We furthermore believe that additional new magnetic properties and functions that have never been observed for conventional metal and metal oxide magnets will appear in mixed ferroferrimagnets composed of Prussian blue analogs.

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[21] Very recently, a double temperature-induced magnetization reversal has been reported for a $\mathrm{YVO_3}$ single crystal at 77 and 95 K [Y. Ren, T.T.M. Palstra, D.I. Khomskii, E. Pellegrin, A.A. Nugroho, A.A. Menovsky, and G.A. Sawatzky, Nature (London) **396**, 441 (1998)]. However, the mechanism is completely different from that in the present system; i.e., the magnetization reversal at 77 K is induced by a first-order structural phase transition in the $\mathrm{YVO_3}$ ferrimagnet. Therefore, this compound does not maintain zero magnetization at that temperature, showing that it has only one compensation temperature.

[22] In this series, parallel spins ($\mathrm{Ni^{II}}$, $\mathrm{Fe^{II}}$, and $\mathrm{Cr^{III}}$) and antiparallel spins ($\mathrm{Mn^{II}}$) can be partially or even completely canceled, depending on the mixing ratio, because $\mathrm{Cr^{III}}$ and either $\mathrm{Ni^{II}}$, $\mathrm{Mn^{II}}$, or $\mathrm{Fe^{II}}$ are linked in an alternating fashion. In this manner, for the members of the series $(\mathrm{Ni}^{\mathrm{II}}_a\mathrm{Mn}^{\mathrm{II}}_b\mathrm{Fe}^{\mathrm{II}}_c)_{1.5}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6]\cdot z\mathrm{H_2O}$ ($S_{\mathrm{Ni}} = 1$, $S_{\mathrm{Mn}} = 5/2$, $S_{\mathrm{Fe}} = 2$, and $S_{\mathrm{Cr}} = 3/2$), I_s is given by $I_s = 2\mu_B|S_{\mathrm{Cr}} + 1.5(S_{\mathrm{Ni}}a - S_{\mathrm{Mn}}b + S_{\mathrm{Fe}}c)|$.

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