The observation of two compensation temperatures in a cobalt-manganese hexacyanochromate

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Abstract

We have prepared a new series of ternary metal Prussian blue analogs, $K^{I}_{a}(Co^{II}_{x}Mn^{II}_{1-x})_{1.5-0.5a}[Cr^{III}(CN)_6]\cdot zH_2O$, incorporating ferromagnetic interaction between Co^{II} and Cr^{III} ions and antiferromagnetic interaction between Mn^{II} and Cr^{III} ions. The material for the composition of $(a, x) = (0.18, 0.39)$ exhibited two compensation temperatures of 34 K and 14 K, i.e., the spontaneous magnetization changed its sign twice with changing temperature. This material is the second example of the bulk magnet exhibiting two compensation temperatures.

Key words:
Ferromagnetism; Ferrimagnetism; compensation temperature; Prussian blue analogs

1. Introduction

Magnetic materials play an important role in modern technology, and various magnets having novel properties are being developed. However, the rational design of new magnetic property is not so easy. Particularly, the control of the thermodynamics of magnetization is difficult. In the classical theory of ferrimagnets, Néel envisaged the possibility that a spontaneous magnetization might change sign at a particular temperature (so-called compensation temperature; T_{comp}) [1]. In the series of our works, we are trying to obtain a magnet exhibiting a compensation temperature with multi-metal Prussian blue analogs. For example, the mixed ferro-ferrimagnet $(Ni^{II}_{x}Mn^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]\cdot 7.5H_2O$ $(0.38 \leq x \leq 0.42)$ showed compensation temperatures according to the prediction of a simple molecular field theory [2,3]. Moreover, we have recently prepared a novel type of magnet exhibiting two compensation temperatures with $(Ni^{II}_{0.22}Mn^{II}_{0.60}Fe^{II}_{0.18})_{1.5}[Cr^{III}(CN)_6]\cdot 7.6H_2O$ [4]. The key to obtaining such a material was the simultaneous incorporation of one antiferromagnetic and two different ferromagnetic interactions through the use of four different spin sources. In the present work, we have observed two compensation temperatures in a new series of cyano-bridged metal assembly, $K^{I}_{a}(Co^{II}_{x}Mn^{II}_{1-x})_{1.5-0.5a}[Cr^{III}(CN)_6]\cdot zH_2O$, incorporating ferromagnetic and antiferromagnetic superexchange interactions.

2. Results and discussion

The $K^{I}_{a}(Co^{II}_{x}Mn^{II}_{1-x})_{1.5-0.5a}[Cr^{III}(CN)_6]\cdot zH_2O$ ($z = 7 \sim 9$) were prepared by reacting mixtures of $CoCl_2$ and $MnCl_2$ aqueous solutions with $K_3Cr(CN)_6$ aqueous solution to yield light pink precipitates. Elemen-

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tal analyses for Co, Mn, and Cr were obtained by inductively coupled plasma mass spectrometry, e.g., calculated for $K^{I}_{0.18}(Co^{II}_{0.39}Mn^{II}_{0.61})_{1.41}[Cr^{III}(CN)_6]\cdot 9H_2O$: Co, 7.1; Mn, 10.3; Cr, 11.4 %, and found: Co, 6.9; Mn, 10.3; Cr, 11.5 %.

Magnetization measurements for the obtained materials were carried out using a Quantum Design MPMS 5 superconducting quantum interference device magnetometer. The observed magnetic properties basically obeyed the theory of the mixed ferro-ferrimagnetism reported in our previous papers [2,3]. For example, the saturation magnetization (M_s) value of 0.5 μ_B for the composition of $(a, x) = (0.18, 0.39)$ is close to the theoretical M_s value of 0.35 μ_B for a mixed ferro-ferrimagnet, assuming the parallel ordering between unpaired electrons on Co^{II} and Cr^{III} ions and antiparallel ordering between those of Mn^{II} and Cr^{III} ions. In addition, the coercive field (H_c) value of 1400 G was larger than the H_c values for $Mn^{II}_{1.5}[Cr^{III}(CN)_6]\cdot 7.5H_2O$ (H_c = 6 G) and $Co^{II}_{1.5}[Cr^{III}(CN)_6]\cdot 7.5H_2O$ (H_c = 400 G). This is because the H_c values for the mixed ferro-ferrimagnets are proportional to $(M_s)^{-1}$. Figure 1 shows the field-cooled magnetization vs. temperature plots for the composition of $(a, x) = (0.18, 0.39)$ in an external magnetic field of 10 G. In the temperature range between 52 K (magnetic critical temperature: T_c) and 34 K, the positive sublattice magnetization dominates. Between 34 K and 14 K, however, the negative sublattice magnetization outweighs the positive magnetization. At temperatures below 14 K, the positive magnetization again dominates. This material thus exhibited two compensation temperatures of 34 K (T_{comp1}) and 14 K (T_{comp2}). Its remanent magnetization vs. temperature plots also showed a similar behavior.

In the case of $(Ni^{II}_{0.22}Mn^{II}_{0.60}Fe^{II}_{0.18})_{1.5}[Cr^{III}(CN)_6]\cdot 7.6H_2O$ reported in our previous paper [4], the appearance of two compensation temperatures could be explained by the simultaneous incorporation of one antiferromagnetic interaction (J_{MnCr}) and two different ferromagnetic interactions (J_{NiCr} and J_{FeCr}) through the use of four different spin sources. In addition, the temperature dependence of magnetization plots was completely calculated by the molecular field theory considering only the superexchange interactions between nearest neighbors as mentioned above. However, the present system has not four-sublattice magnetizations but three-sublattice magnetizations. In the system of three-sublattice magnetization, two compensation temperatures cannot be caused by only the superexchange interactions between nearest neighbors, i.e., J_{CoCr} and J_{MnCr}. Recently, the possibility of two compensation temperatures has been theoretically discussed in a variety of ferrimagnetic systems [5–7]. Based of these theoretical studies, we are now considering that the possible reasons of the appearance of two compensation temperatures in the present system are as follows: (1) the superexchange interactions between second nearest neighbors (2) single-ion anisotropy of Co^{II} ion (3) the contamination of other sublattice magnetizations due to the divalent ions coordinated by water molecules.

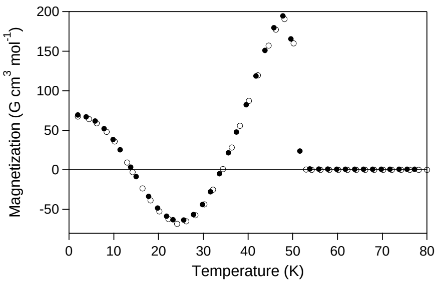

Fig. 1. Magnetization vs. temperature curves for $K^{I}_{0.18}(Co^{II}_{0.39}Mn^{II}_{0.61})_{1.41}[Cr^{III}(CN)_6]\cdot 9H_2O$:(●) field-cooled magnetization obtained with decreasing temperature (80 K→2 K) in an external magnetic field of 10 G; (○) remanent magnetization obtained with increasing temperature (2 K→80 K) after the temperature was lowered in the applied magnetic field of 10 G.

Multi-metal Prussian blue analogs have a possibility showing new magnetic properties and functionalities because the fcc structure of the Prussian blue analogs is maintained even when the metal ions are substituted. For example, we have demonstrated a photo-induced magnetic pole inversion [8] and an inverted magnetic hysteresis loop [9].

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