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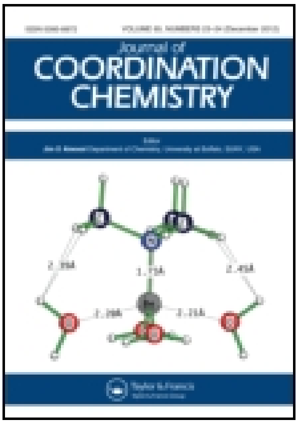

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Charge-transfer-induced spin transition in $K_{0.28}Co_{1.36}[Fe(CN)_6]\cdot XH_2O$ with different annealing temperatures

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Charge–transfer-induced spin transition in $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$ with different annealing temperatures

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The Prussian blue analog $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$ was prepared by standard chemical co-precipitation. The precipitate was filtered and dried in a vacuum oven at room temperature, 80°C, and 120°C. The powder X-ray diffraction measurement indicates a typical face-centered cubic pattern. The diffraction peaks show a slight shift to higher angle with increasing annealing temperatures, a signature of lattice contraction, which is mainly related to the inner charge transfer from Fe^{III} to Co^{II}. The value of $\chi \cdot T$ is variable and dependent on temperature. The temperature dependence of χ^{-1} shows a large deviation from the Curie–Weiss law. The behavior could result from a charge-transfer-induced spin transition. Isothermal magnetization curves also suggest that the inner charge-transfer spin transition depends on the annealing temperature.

Keywords: Two states; Lattice contraction; Charge transfer; Spin transition

1. Introduction

Molecular magnetism has been extensively studied [1–5]. In some molecule-based magnets, external stimulations such as temperature, photo, and magnetic fields, induced a spin crossover between a high-spin state and a low-spin state [5–8]. As one member of the tunable spin molecule-based magnet family, Prussian blue analog $A_iCo_j[Fe(CN)_6]_k \cdot XH_2O$, where A is an alkali cation, was extensively studied for photo-induced spin crossover [7–14]. Hashimoto *et al.* studied photo-induced magnetic properties of a series of $K_iCo_j[Fe(CN)_6]_k \cdot XH_2O$ compounds by varying the K/Co ratio [12, 13]. The photo-induced magnetic material was based on the charge-transfer-induced spin transition (CTIST) between two states, one consisting of the $Fe^{II}(t_{2g}^6e_g^0$, LS, $S=0)$–CN–$Co^{III}(t_{2g}^6e_g^0$, LS, $S=0)$ and the other consisting of $Fe^{III}(t_{2g}^5e_g^0$, LS, $S=1/2)$–CN–$Co^{II}(t_{2g}^5e_g^2$, HS, $S=3/2)$ [12–14]. Visible light illumination induced electron transfer from Fe^{II} to Co^{III}. The inverse process of electron transfer in Co^{II}–Fe^{III} Prussian blue analog was caused by cooling [15] at low temperature or heating above 80°C [16, 17]. Park *et al.* [15] reported that $K_{0.4}Co_{1.3}[Fe(CN)_6] \cdot XH_2O$ exhibits cooling induced

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charge-transfer spin transition from Fe^{III} to Co^{II}. The compound consisted of $Fe^{III}(t_{2g}^5e_g^0$, LS, $S=1/2)$–CN–$Co^{II}(t_{2g}^5e_g^2$, HS, $S=3/2)$ at room temperature but turned to the state consisting of $Fe^{II}(t_{2g}{}^6e_g{}^0$, LS, $S=0)$–CN–$Co^{III}(t_{2g}^6e_g^0$, LS, $S=0)$ at low temperature [15]. On heating above 80°C, the Co–Fe Prussian blue analog underwent an inner charge transfer from Fe^{III} to Co^{II} to form $Co^{III}Co^{II}$ ferrocyanide [16, 17]. Oxidation of cobalt also changed from high-spin Co^{II} to low-spin Co^{III}. The CTIST phenomenon in Co–Fe cyanides has been reported; however, the effects of cooling after annealing have not been seen. In this article, we report the charge-transfer spin transition of $K_{0.4}Co_{1.3}[Fe(CN)_6]\cdot XH_2O$ samples annealed at room temperature, 80°C and 120°C, respectively.

2. Experimental

The $K_{0.28}Co_{1.36}[Fe(CN)_6]\cdot XH_2O$ powder sample was prepared from a solution reaction of $Co(NO_3)_2\cdot 6H_2O$ and $K_3[Fe(CN)_6]$ by controlling the KNO_3 concentration. An aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ (0.1 mmol mL^{-1}) was then slowly added to a mixed aqueous solution of $K_3[Fe(CN)_6]$ (0.05 mmol mL^{-1}) and KNO_3 (0.5 mmol mL^{-1}), which produced a cobalt iron polycyanide precipitate. This precipitate was filtered and dried in a vacuum oven at room temperature, 80°C, or 120°C, yielding a purple microcrystalline powder.

X-ray fluorescence spectrometry and powder X-ray diffraction using Cu-Kα radiation were used to characterize the structures of the samples. Magnetic properties were investigated with a vibrating sample magnetometer integrated in a physical property measurement system (PPMS-9, Quantum Design) up to 50,000 Oe from 5 K to 300 K. According to X-ray fluorescence spectrometry, the metal ratios (K : Co : Fe) found for the samples are close to 0.28 : 1.36 : 1, supporting the expected formula unit, $K_{0.28}Co_{1.36}[Fe(CN)_6]\cdot XH_2O$.

3. Results and discussion

3.1. *Powder X-ray diffraction*

Figure 1 shows X-ray diffraction patterns of $K_{0.28}Co_{1.36}[Fe(CN)_6]\cdot XH_2O$ annealed at room temperature, 80°C, and 120°C, respectively. The measurements indicated face-centered cubic patterns of compounds annealed at different temperatures. The diffraction peaks show a little shift to higher values of 2θ with increasing annealing temperatures. The lattice parameters are 10.374(3), 10.256(5), and 10.114(4) Å for samples annealed at room temperature, 80°C, and 120°C, respectively. This is a signature of lattice contraction, related to the inner charge transfer from Fe^{III} to Co^{II}. The Co to cyanide bond in Fe^{III}–CN–Co^{II} is much weaker than that in Fe^{II}–CN–Co^{III}. The strengthening of the Co–N interaction for low-spin Co^{III} reduces the inter-atomic distance N–Co^{III}. A certain contribution to the cell contraction is also due to the smaller Fe^{II}–C distance by a stronger bonding interaction. Therefore, the Fe^{II}–CN–Co^{III} length is smaller than that of Fe^{III}–CN–Co^{II}. For samples annealed at room

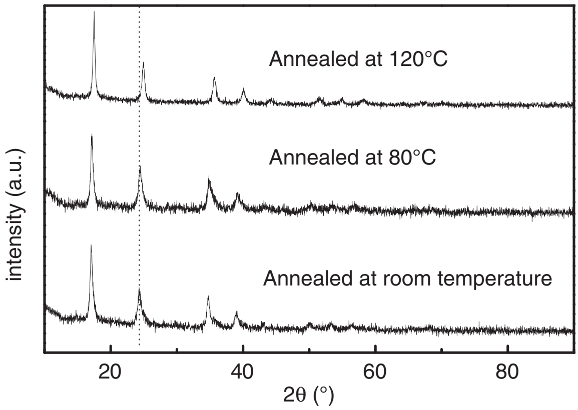

Figure 1. X-ray diffraction patterns of $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$ annealed at room temperature, 80°C, and 120°C.

temperature, 80°C, and 120°C, the Fe–Co cyanide bond distances are 5.187(1), 5.128(2), and 5.057(2) Å, respectively. With the annealing temperatures increasing from room temperature to 120°C, the Fe–Co cyanide bond distances decrease as much as 0.13 Å. The lattice contraction mainly arises from inner charge transfer from Fe^{III} to Co^{II}.

3.2. *DC magnetization*

In cyanide complexes, the magnetic order is established by a super-exchange interaction through CN bridges. At low temperature the unpaired electrons of the metallic centers are responsible for the magnetic interaction. For Prussian blue analogs, iron coordinated to carbon of CN^- is always low-spin. In $K_{0.28}Co^{II}{}_{1.36}[Fe^{III}(CN)_6] \cdot XH_2O$, low-spin Fe^{III} has a configuration t_{2g}^5, while high-spin Co^{II} has a configuration $t_{2g}^5e_g^2$. The interaction between the t_{2g} orbital of Fe^{III} and the t_{2g} orbital of Co^{II}, which are overlapping with each other, would lead to antiferromagnetic interaction. On the other hand, interaction between the t_{2g} orbital of Fe^{III} and the e_{2g} orbital of Co^{II}, which are mutually orthogonal, will give ferromagnetic interaction. The compound shows a combined effect of both an antiferromagnetic interaction and a ferromagnetic one. In general, the antiferromagnetic contribution is much more effective than ferromagnetic in Prussian blue analogs. Therefore, the magnetic coupling between Co^{II} and Fe^{III} in $K_{0.28}Co^{II}{}_{1.36}[Fe^{III}(CN)_6] \cdot XH_2O$ is antiferromagnetic, and a ferrimagnetic order may be present.

Magnetic susceptibility measurements were performed in the cooling mode at $0.5\,K\,min^{-1}$ from 5 to 300 K. The temperature dependence of $\chi \cdot T$ for $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$ is shown in figure 2. The value of $\chi \cdot T$ is variable and dependent on temperature. For all the samples, when the temperature is lowered, the $\chi \cdot T$ values decrease from 300 to 15 K and then sharply increase to reach a maximum value around 9 K, then decreasing as temperature is decreased further, reflecting the ferrimagnetic nature of the materials. As the temperature is decreased from 300 to 80 K, the $\chi \cdot T$ value of the sample annealed at room temperature decreased from 0.011 to $0.0086\,emu\,KOe^{-1}\,g^{-1}$. The temperature behavior of the $\chi \cdot T$ product between

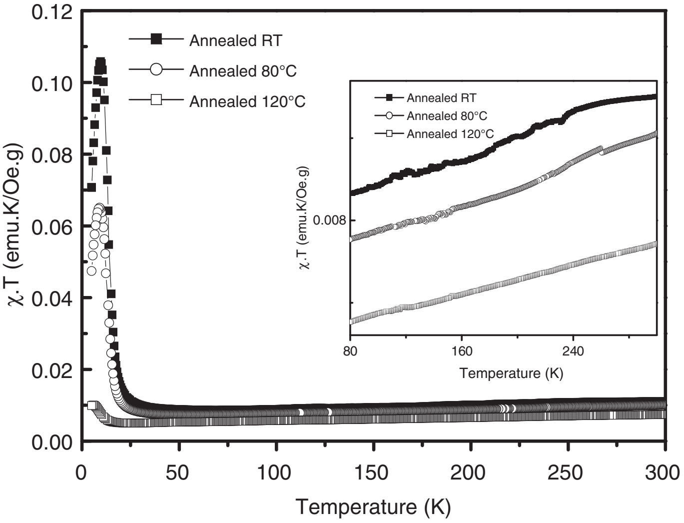

Figure 2. The temperature dependence of $\chi \cdot T$ of $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$ annealed at room temperature, 80°C, and 120°C at 500 Oe field.

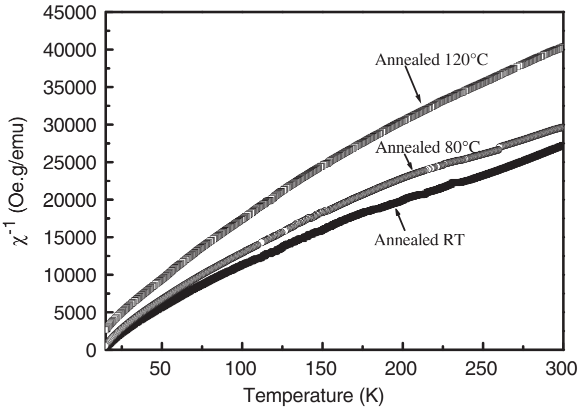

Figure 3. Temperature dependence of χ^{-1} for $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$ annealed at room temperature, 80°C, and 120°C.

300 and 80 K is due to a cooling activated electron-transfer spin transition. With increase in annealing temperature from room temperature to 120°C, the $\chi \cdot T$ value below 15 K decreases, because heating above 80°C also activates a CTIST. For example, the maximum values of $\chi \cdot T$ are 0.1062, 0.6507, and 0.0099 emu K Oe^{-1} g^{-1} for the samples annealed at room temperature, 80°C, and 120°C, respectively. Therefore, figure 2 shows that both heating above 80°C and cooling from 300 to 80 K may induce a CTIST in $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$.

The temperature dependence of χ^{-1} from 15 to 300 K is shown in figure 3. The curves all over the temperature ranges are arc-shaped, large deviation from the Curie–Weiss law.

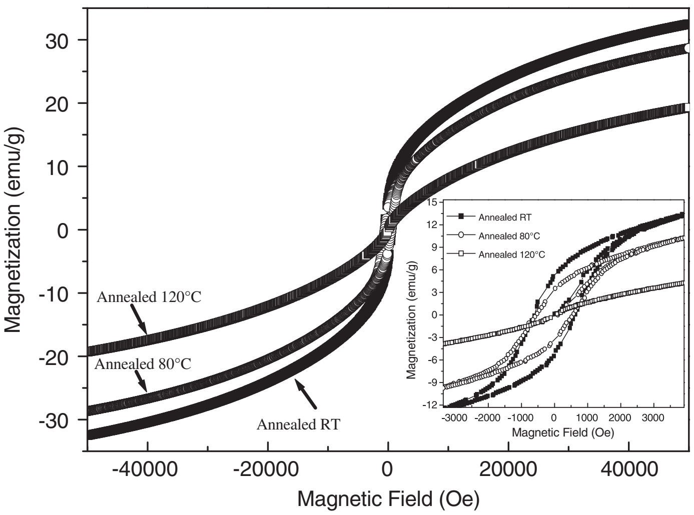

Figure 4. The isothermal magnetization curves at 5 K for $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$ annealed at room temperature, 80°C, and 120°C.

Cooling from 300 to 80 K or heating above 80°C produces a reduction of antiferromagnetic interaction. This behavior is due to the existence of two states in the material, with one of them being $Fe^{III}(t_{2g}^5e_g^0$, LS, $S=1/2)$–CN–$Co^{II}(t_{2g}^5e_g^2$, HS, $S=3/2)$ and the other being $Fe^{II}(t_{2g}^6e_g^0$, LS, $S=0)$–CN–$Co^{III}(t_{2g}^6e_g^0$, LS, $S=0)$, indicating a CTIST of the $Fe^{III}(t_{2g}^5e_g^0$, LS, $S=1/2)$–CN–$Co^{II}(t_{2g}^5e_g^2$, HS, $S=3/2)$ state to the lower spin $Fe^{II}(t_{2g}^6e_g^0$, LS, $S=0)$–CN–$Co^{III}(t_{2g}^6e_g^0$, LS, $S=0)$ state.

Isothermal magnetization curves at 5 K are shown in figure 4. Samples annealed at room temperature and 80°C exhibit hysteresis loops with a coercive field of 622 Oe and 557 Oe, respectively. The value of the coercive field decreases with increasing annealing temperature from room temperature to 80°C. In the case of the sample annealed at 120°C, there are no coercive field and remanence, and the isothermal magnetization does not show a hysteresis loop. The isothermal magnetization curves also indicate that the inner charge transfer leads to a parallel sum reduction of Fe^{III} and Co^{II}.

4. Conclusion

We obtained $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$ to show the CTIST phenomenon. Powder X-ray diffraction indicated a typical face-centered cubic pattern. The cell contraction is generated by formation of Fe^{II}–CN–Co^{III} chains with a shorter length. Furthermore, the CTIST phenomenon between two states has also been observed in magnetic measurements. The value of $\chi \cdot T$ is variable and dependent on temperature. The curves of the temperature dependence of χ^{-1} are arc-shaped, with large deviation from the Curie–Weiss law. The isothermal magnetization curves also show that heating above 80°C leads to a reduction in the amount of Fe^{III} and Co^{II}. Both heating above 80°C and cooling from 300 to 80 K may induce a CTIST in $K_{0.28}Co_{1.36}[Fe(CN)_6] \cdot XH_2O$; electronic and spin states of iron and cobalt ions strongly depend on the temperature.

Temperature-dependent CTIST gives an additional spin control mechanism that might be useful for modern magnetic applications.

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