

Phase transitions in mixed-valence potassium manganese hexacyanoferrate Prussian blue analogue: Heat capacity calorimetric study[☆]

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Abstract

Phase transitions in $K_{0.2}Mn_{0.66}^{II}Mn_{1.44}^{III}[Fe_{0.2}^{II}Fe_{0.8}^{III}(CN)_6]O_{0.66}(CH_3COO)_{1.32} \cdot 7.6H_2O$ —a mixed valence PB analogue have been investigated with the help of heat capacity calorimetry under 0–90 kOe magnetic fields in the 1.8–300 K temperature range. Two heat capacity anomalies at 2.1 and 7.5 K have been detected, which correspond to ferromagnetic and ferrimagnetic transitions, respectively. The magnitudes as well as the position of these thermal anomalies have varied with changing magnetic field. The estimated zero-field magnetic entropy amounted to $29.2 J K^{-1} mol^{-1}$, which is close to the expected value ($33.7 J K^{-1} mol^{-1}$). The uniaxial zero-field splitting parameter is estimated to be $D/k_B = 14.7 K$. A comparatively stronger antiferromagnetic interaction seems to lead to the magnetic transition around 7.3 K, whereas a weaker ferromagnetic interaction gives rise to the thermal anomaly at 2.1 K. The present results on magnetic phase transitions are in complete agreement with the earlier observations made through magnetic studies. Additionally, a glass transition at 194 K has been observed in the heat capacity study presumably due to freezing of the orientational motion of the H_2O molecules present in the material. This phenomenon is reflected into the temperature dependence of the estimated Fe^{III} and Fe^{II} concentrations in the present material obtained earlier through Mössbauer spectroscopy.

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1. Introduction

Molecular systems exhibiting tuned reversibility in their physical properties caused by change in external parameter offer an appealing perspective for the realization of molecular-scale electronic devices [1]. In this light the mixed valence Prussian blue (PB) analogues, $M_xA_y^{II}[B^{III}(CN)_6] \cdot nH_2O$, (M—alkali metal; A and B—divalent and trivalent transition metal ions, respectively) have been drawing active

research interest in the field of molecular magnetism for their technological application potentials [2–15]. These materials have quasi-degenerate electronic states whose energy difference frequently approaches the thermal energy, making the transition between them on application of an appropriate external stimulus, e.g., temperature [4,8–10], pressure [5,11,12], light [13,14], humidity [15] involving internal metal-to-metal charge transfer ($A^{II}-N-C-B^{III} \leftrightarrow A^{III}-N-C-B^{II}$) mediated by the cyanide bridge. In these PB analogues, usually the coupling of A and B metals becomes antiferromagnetic when the spin-containing orbitals of magnetic ions are of same symmetry, otherwise ferromagnetic coupling appears when the orbitals are orthogonal [16]. Variations of A and B metal ions as well as the introduction of additional defects/water or solvent molecule clusters

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change the type, strength and 3-D topology of the magnetic coupling [9,17]. These materials exhibit various magnetic properties depending on their transition metal combinations, e.g., high T_C magnet [3,4], magnetic pole reversal [5], spin glass behavior [5], magnetocaloric effect [7]. The coexistence of long range magnetic ordering, thermal hysteresis and electron-transfer properties usually observed in these PB analogues makes them attractive for the design of molecule-based magnets modulating the nature of the interaction between the paramagnetic ions through the cyanide bridge, sensitive to external perturbations, e.g., temperature, light irradiation, pressure.

Several interesting bimetallic transition metal Prussian blue type hexacyanide 3-D network structures with interesting magnetic properties have been reported so far. $V[Cr(CN)_6]_{0.86} \cdot 2.8H_2O$ complex has exhibited a very high Curie temperature (315 K) [3]. $Co_x^{II}[Fe^{III}(CN)_6]_y \cdot nH_2O$ and its alkali-doped analogues have exhibited the foremost incidences of photo-induced [18] and pressure-induced [11] metal-to-metal electron transfer and magnetism in a 3-D compound. Another important member of the Prussian blue family— $Mn_x^{II}[Fe^{III}(CN)_6]_y \cdot nH_2O$ was reported to be ferrimagnetic with T_N at 9 K [19]. Alkali-doped rubidium manganese hexacyanoferrate— $RbMn^{II}[Fe^{III}(CN)_6]$ has recently been reported to be ferrimagnetic below 12 K from the magnetic measurements, along with a thermal spin transition associated with a broad thermal hysteresis loop of 73 K, due to a charge transfer phenomenon between Fe and Mn ions, and the Jahn–Teller distortion of the Mn^{III} ions [8,21–25]. A photo-induced phase transition has also been observed in this compound [26]. In these Mn–Fe cyanides the electronic state of Mn changes between trivalent high spin state at low temperatures and divalent high spin state at high temperatures caused by a metal-to-metal charge transfer between Mn and Fe ions, and a Jahn–Teller distortion of Mn^{III} ion occurs in the LT phase [20,21]. Some other heterobimetallic PB analogues were also reported to exhibit photo-induced metal-to-metal electron transfer phenomenon e.g., $Cu^{II}-Mo^{IV} \leftrightarrow Cu^I-Mo^V$ [27] and $W^{IV}-Co^{III} \leftrightarrow W^V-Co^{II}$ [28]. Literature reports that the spin transitions in these PB metal-cyanides have so far been reported to commonly originate from the metal-to-metal charge transfer phenomenon, however, no low spin \leftrightarrow high spin transition has been seen so far.

The characteristic individual magnetic behaviors as well as the metal-to-metal charge-transfer capabilities in the various PB analogues are related with significant changes within the structures that appear to be associated with the synthetic methods adopted [9]. Thus, in an attempt to obtain one alkali-mixed Mn–Fe type PB analogue through a different synthetic route, we have obtained potassium manganese hexacyanoferrate— $K_{0.2}Mn_{0.66}^{II}Mn_{1.44}^{III}[Fe_{0.2}^{II}Fe_{0.8}^{III}(CN)_6]O_{0.66}(CH_3COO)_{1.32} \cdot 7.6H_2O$ (KMnFe in short) [10]. From the magnetic studies of this compound in SQUID magnetometer a para- \leftrightarrow ferrimagnetic transition below ~ 10 K was detected, and the existence of a weak ferromagnetic transition below 3 K was hypothesized.

Mössbauer spectroscopic studies of this compound in 1–300 K range demonstrated the varying presence of both Fe^{III} and Fe^{II} ions in low-spin states. Quantitative analysis of the amount of Fe^{III} and Fe^{II} ions, and their temperature dependence observed for the present material exhibited the existence of a metal-to-metal electron transfer phenomenon between Mn and Fe ions [$Fe^{III} (t_{2g}^5, S = \frac{1}{2})-CN-Mn^{II} (t_{2g}^3 e_g^2, S = 5/2) \leftrightarrow [Fe^{II} (t_{2g}^6, S = 0)-CN-Mn^{III} (t_{2g}^3 e_g^1, S = 2)]$].

As heat capacity is sensitive to a change in the degree of short-range and long-range ordering, one can examine the existence of phase transition(s) and/or any anomaly by measuring the heat capacity [29]. The presence of a large number of atoms in a molecule gives rise to a large lattice heat capacity even at low temperatures, which often makes it difficult to separate the magnetic heat capacity contribution without ambiguity. There are only few reports on the heat capacity calorimetric investigations of the magnetic transitions in PB analogues. By measuring the molar heat capacity of $RbMn[Fe(CN)_6]$, Tokoro et al. observed a λ -type thermal anomaly owing to ferromagnetic phase transition at 11 K, assumed to be due to the valence delocalization mechanism [24]. In another case of heat-capacity study of cyanide-bridged bimetallic complexes, Larionova et al. observed λ -type heat-capacity peak due to ferromagnetic transition at 50.5 K in $[Mn_2(H_2O)_5Mo(CN)_7] \cdot 4H_2O$ [30]. Presently, we have employed the heat capacity calorimetry to investigate phase transitions in KMnFe in order to establish our understanding of magnetic phase transitions from previous magnetic studies, and the results obtained are discussed in the present paper. The present heat capacity results corroborate the earlier made observations and predictions on the nature of magnetic interactions in KMnFe [10].

2. Experimental details

The polycrystalline $K_{0.2}Mn_{0.66}^{II}Mn_{1.44}^{III}[Fe_{0.2}^{II}Fe_{0.8}^{III}(CN)_6]O_{0.66}(CH_3COO)_{1.32} \cdot 7.6H_2O$ material used for the heat capacity measurements was of the same batch used previously for the magnetic measurements [10]. Two calorimeters were employed for the heat capacity measurement of the sample to cover different temperature regions as well as to study the heat capacity under external magnetic field at lower temperatures. The heat capacity measurements between 1.8 and 30 K in the $H = 0-90$ kOe magnetic field range were carried out with a commercial calorimeter that uses a relaxation method (Quantum Design, PPMS 6000). Polycrystalline materials (mass = 5.5994×10^{-3} g) were pressed into small pellet and the pellet was used for the heat capacity measurements in PPMS. The measured heat capacity in PPMS calorimeter involves contributions from both the addenda (sample holder + grease) and the sample. The sample heat capacities were determined by subtracting those of the addenda from the measured values. The temperature

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