Magnetic properties and neutron diffraction study of (Ni$_x$Mn$_{1-x}$)$_3$[Cr(CN)$_6$]$_2$ molecule-based magnets

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Abstract. Neutron diffraction measurements were performed on (Ni$_x$Mn$_{1-x}$)$_3$[Cr(CN)$_6$]$_2$·zD$_2$O ($x = 0, 0.38$ and $1$) powders above and below the Curie temperature $T_C$. The crystal structure, including D-sites, was fully described. Neutron diffraction experiments revealed magnetic contribution for all compounds. Magnetization measurements and elastic neutron diffraction of Mn$_3$[Cr(CN)$_6$]$_2$ indicate magnetic structure consisting of Mn and Cr sublattices with antiparallel magnetic moments $\mu_{\text{Mn}} = 3.790 \ \mu_B$ and $\mu_{\text{Cr}} = -1.375 \ \mu_B$ leading to overall ferromagnetic ordering below the Curie temperature $T_C = 64.5$ K. Very weak magnetic contribution was observed on investigated Ni$_3$[Cr(CN)$_6$]$_2$ and (Ni$_{0.38}$Mn$_{0.62}$)$_3$[Cr(CN)$_6$]$_2$ powders at 1.6 K and at 60 K respectively. Our results are compared and discussed with magnetization measurements of $M(T)$ and heat capacity measurements $C(T)$ in zero magnetic field and magnetic fields up to $\mu_0 H = 5$ T.

1. Introduction

Prussian blue analogues (PBA) build a large family of cubic systems. One possible structure displays A$_3$[B(CN)$_6$]$_2$·zH$_2$O stoichiometry and the crystal structure is face-centered (fcc) [1]. To analyze magnetic properties of PBA two simplifications can be made: (a) only the superexchange interactions between the nearest neighbor metal A and B ions have to be considered; (b) if the magnetic orbital symmetries of the metal ions are the same, the super-exchange interaction is antiferromagnetic ($J_{\text{AF}}$); conversely when their magnetic orbital symmetries are different, the super-exchange interaction is ferromagnetic ($J_{\text{F}}$). The B atom, which is surrounded by the carbon atoms of six cyanide ligands, is in a large ligand field [2]. Mean field, ligand field and exchange models have been already tested on TM$_2^+$[Cr$^{III}$(CN)$_6$]$_2$·zH$_2$O system, where TM$^{2+}$ is 3d ion [1, 2]. Recently a new type of molecule-based magnet, the mixed ferro – ferrimagnet (Ni$_x$Mn$_{1-x}$)$_3$[Cr(CN)$_6$]$_2$, has been discovered [3]. These compounds accommodate both $J_{\text{AF}}$ and $J_{\text{F}}$ interactions and their magnetic properties can be controlled by changing the compositional factor $x$. In the classical theory of ferrimagnets, Néel envisaged the possibility that the spontaneous magnetization might change sign at a particular temperature – the compensation temperature $T_{\text{comp}}$ [4] like in case of (Ni$_x$Mn$_{1-x}$)$_3$[Cr(CN)$_6$]$_2$ system [3].

Structural and magnetic properties of PBA were studied by neutron diffraction (ND) only rarely. First results obtained by ND are mentioned in [1]. Ligand field analysis is based on spin density maps obtained from polarized spin ND [6]. Powders neutron diffraction of Fe$_4$[Fe(CN)$_6$]$_3$·z(H,D)$_2$O reveals
two structurally distinguishable kinds of water – coordinated to Fe$^{III}$ and additional water present as isolated molecules at the center of the unit cell octants or as water molecules connected by hydrogen bonds to the coordinated ones. Magnetic contribution to the neutron intensities below $T_C = 5.6$ K corresponds to the parallel alignment of high-spin Fe$^{III}$ with $S = 5/2$ [7]. Ordered site moments obtained from the ND study of Fe$^{III}$[Fe$^{III}$(CN)$_6$]-4H$_2$O confirm the ferromagnetic ordering of Fe$^{III}$ ($S = 5/2$) at (0, 0, 0) and Fe$^{III}$ ($S=1/2$) at (1/2,1/2,1/2) site moments [8]. X-ray and ND show structured diffuse scattering indicative of partially correlated (rather than random) substitutions of [Mn$^{III}$(CN)6] ions by (H$_2$O)$_6$ clusters in Mn$^{II}$(Mn$^{III}$(CN)6)$_2$.zH$_2$O. Magnetic measurements and ND indicate a ferrimagnetic structure below the critical temperature $T_C = 35.5$ K [9]. The various scattering contributions (e.g., nuclear diffuse, nuclear Bragg, and magnetic Bragg) were estimated from the observed neutron diffraction patterns of Cu$_{0.73}$Mn$_{0.77}$[Fe(CN)$_6$].zH$_2$O. The Rietveld refinement technique showed an antiferromagnetic ordering of Mn moments with respect to the Cu as well as the Fe moments [10]. The deuterium positions in the crystal structure of Dy[Fe(CN)$_6$].4D$_2$O were localized and the complete crystal structure ($Cmcm$ space group) was refined using Rietveld method [11]. ND revealed that the magnetic structure consists of Fe and Dy sublattices which are coupled antiferromagnetically leading to overall ferrimagnetic ordering with the Curie temperature $T_C = 3.7$ K. While for Fe-atoms the y-component of magnetic moment is large and the z-component is negligible, in the case of Dy-atoms the x-and the y-magnetic moment components are large and the arrangement of magnetic moments on Dy-sublattice is non-collinear [12]. Here we present our study of magnetic properties and neutron diffraction study performed on Ni$_3$[Cr(CN)$_6$]$_2$ ferromagnet, Mn$_3$[Cr(CN)$_6$]$_2$ ferrimagnet and (Ni$_{0.38}$Mn$_{0.62}$)$_3$[Cr(CN)$_6$]$_2$ mixed ferro-ferrimagnet.

2. Experimental, results and discussion

Neutron diffraction data were taken from two sets of (Ni$_{1-x}$Mn$_x$)$_3$[Cr(CN)$_6$]$_2$.zD$_2$O powders on E9 ($\lambda = 1.79734$ Å, HCME-Berlin) for $x = 0, 1$ at $T = 2$K, 100 K and on G4.1 ($\lambda = 2.42500$ Å, LLB Saclay) for $x = 0, 0.38, 1$ at different temperatures below $T = 70$ K. Expected crystal structure $fcc$ space group $Fm-3m$ was confirmed for all samples but remarkable magnetic contribution was observed only on Mn$_3$[Cr(CN)$_6$]$_2$ samples and in this paper we concentrate to this type of compound. The H atoms were replaced with D in the process of samples preparation. The number of z fluctuated between 12 and 15 but in majority cases was close to 12. The high value of background observed on data from E9 indicates that D$_2$O molecules are substituted by H$_2$O molecules during the ageing of the samples and

![Figure 1](image1.png)  
**Figure 1.** The crystal structure ($Fm-3m$ space group, $a = 10.730$ Å) was refined by the Rietveld method with conventional parameters $R_{wp} = 29.4$ and $\chi^2 = 2.418$.

![Figure 2](image2.png)  
**Figure 2.** Marked area shows one possible arrangement of D$_2$O molecules in crystal structure of Mn$_3$[Cr(CN)$_6$]$_2$.zD$_2$O.
incoherent scattering from H contributes to background (Fig.1.). Location of building units (CrC₆ octahedron, D₂O water molecules and other atoms were taken as isolated) in the cell was performed by the direct-space method using reverse Monte-Carlo approach (Fox [13]). The incoherent scattering resulted in extension of the time of measurement but finally good statistic was obtained and the crystal structure, including D-sites, was fully described by the Rietveld refinement technique (Fig.1.). In order to avoid the replacement of D₂O by H₂O we kept the samples wet for G4.1 experiment. This strategy leads to lower background but a secondary phase (ice made of D₂O) was detected at low temperature Fig.5.

Magnetization $\mu$ of all samples was measured on commercial MPMS-SQUID magnetometer in temperature range from 1.8 K to 300 K and magnetic fields with induction up to 5 T. The Curie temperature $T_C = 64.5$ K, determined as a minimum of $d(\mu(T)/dT)/dT$ curves, is the same (Fig.3.) for Ni₃[Cr(CN)₆]₂ and Mn₃[Cr(CN)₆]₂ systems which is consistent with [3] and the same results we obtained on both sets of samples. ND revealed higher degree of internal disorder for Ni₃[Cr(CN)₆]₂.

**Figure 3.** Magnetization curves were measured in low magnetic field equal to magnetic field of earth with magnetic induction $B = 0.06$ mT.

**Figure 4.** Effects of applied magnetic field on magnetic transition in the mixed ferri-ferromagnetic system.

**Figure 5.** Neutron diffraction patterns of Mn₃[Cr(CN)₆]₂: i.) taken at 1.6 K containing secondary phase – ice, ii) intensity difference showing development of magnetic contribution.

**Figure 6.** Observed and calculated magnetic contributions. The magnetic contribution was refined by Rietveld method with conventional parameters $R_{wp} = 33.9$ and $\chi^2 = 9.65$. 
nuclear Bragg peaks are much wider than for Mn$_3$[Cr(CN)$_6$]$_2$ with relatively sharp Bragg peaks (Fig.1.). Magnetic properties reflect the internal disorder; Ni$_3$[Cr(CN)$_6$]$_2$ is sensitive to ageing, $T_C$ can be lower about 10 K for old-relaxed sample and maximum in zero-field-cooled $\mu$ [4] is usually attributed to cluster-like behaviour in magnetically ordered state. In contrast to [3] value of $T_C = 71$ K is much higher than for samples with $x = 0, 1$. One source of disorder is substitution of Ni for Mn which can lead to homogenous system with random i.e more isotropic distribution of Ni or to inhomogeneous system with Mn-rich and/or Ni-rich region. The small peak in $\mu(T)$ below $T_C$ of sample with $x = 0.38$ following by a flat maximum can indicate inhomogeneous system and clustering in the sample (Fig.3.). This sample exhibits $T_{\text{comp}} = 14.2$ K in $\mu(T)$ measured in very low field. Saturated magnetization $\mu_s = 5.02$ $\mu_B$ of sample with $x = 0.38$ was smaller than $\mu_s = 10.70$ $\mu_B$ for ferromagnetic sample with $x = 1$ and $\mu_s = 8.46$ $\mu_B$ for ferrimagnetic sample with $x = 0$.

Heat capacity was measured on PPMS system from 1.8 K to 300 K and magnetic fields with induction up to 9T. Magnetic transition is accompanied by a sharp peak in heat capacity $C/T$ both samples with $x = 0$ and 1. The applied magnetic field shifts the peak to higher temperatures and smears it out as it is typical for ferri- or/and ferromagnetic systems. In the case of ferri-ferromagnetic system ($x = 0.38$) the peak is quite broad and it’s position is not affected by magnetic field. The second small local maximum can indicate clustering in the sample (Fig.4.).

In the case of Ni$_3$[Cr(CN)$_6$]$_2$ very weak magnetic contribution was observed at 1.6 K, probably due to a distribution of magnetically ordered domains. Magnetization measurements of sample with mixed ferro-ferrimagnet revealed a maximum at about 60 K and low value of $\mu$ at $T = 2$ K (Fig.3.). ND measurements performed on this sample at 60 K revealed only spoors of magnetic contribution. Strong magnetic contribution was observed on Mn$_3$[Cr(CN)$_6$]$_2$ for temperatures below $T_C$ (see Fig.3.) and appeared only on allowed nuclear reflections – no additional reflections were observed on forbidden nuclear Bragg peaks. Diffraction peaks (222), (400), (422) and (440) with magnetic contribution comparable with experimental error were excluded from refinement of magnetic contribution $I_{2K} - I_{70K}$ (Fig.5) using fullprof program. Magnetization and elastic neutron diffraction measurements (Fig.5.) of Mn$_3$[Cr(CN)$_6$]$_2$ indicate magnetic structure consisting of Mn and Cr sublattices with antiparallel magnetic moments $\mu_{\text{Mn}} = 3.79$ $\mu_B$ and $\mu_{\text{Cr}} = -1.37$ $\mu_B$ leading to overall ferrimagnetic ordering below $T_C = 64.5$ K with magnetic moments on 4a(Mn) and 4b(Cr) – sites.

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