

14th Czech and Slovak Conference on Magnetism, Košice, Slovakia, July 6–9, 2010

# Magnetic Properties of $(\text{Cu}_x\text{Mn}_{1-x})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$ Complexes

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Magnetization measurements were performed on the  $(\text{Cu}_x\text{Mn}_{1-x})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  molecule-based magnets where  $x = 0.0, 0.2, 0.25, 0.3, 0.35, 0.4, 0.6, 0.8$  and  $1.0$ . Both the Curie temperature and saturated magnetization at first decrease with increasing value of  $x$  reaching the minimal value of  $T_C = 49.7$  K and  $0.17 \mu_B$  for  $x = 0.2$  and then increase with substitution. The pronounced hysteretic behavior between zero-field cooled and field cooled regimes was observed for all samples. Magnetization changes the sign of magnetic polarization in zero-field cooled magnetization curve at the compensation temperature  $T_{\text{comp}} = 16$  K for sample with  $x = 0.4$ . Our results indicate that the system behaves as mixed-ferri-ferromagnetic system.

PACS numbers: 75.30.Kz, 75.30.Cr

## 1. Introduction

Prussian blue analogues (PBA) are subject of increasing interest mostly because of the possibility to produce molecule — based magnets working at room temperature and because of sensitivity of their magnetic properties on different types of external stimuli. PBA build a large family of cubic systems with face-centered (fcc) crystal structure [1, 2]. The magnetic coupling in these systems is determined by super-exchange interaction between metal ions  $A^{2+}$  and  $B^{\text{III}}$  mediated through three dimensional network of C–N bridges, resulting in 3D magnetic ordering with transition temperatures  $T_C$  up to 376 K depending on the nature of metal ions [2]. In relation to the Goodenough–Kanamori rule [3] two mechanisms should be taken into account for superexchange interactions: kinetic exchange mechanism ( $J_{\text{KE}}$ ) mediated directly via overlapping orbitals and potential exchange mechanism ( $J_{\text{PE}}$ ) mediating interaction between orthogonal magnetic orbitals. The  $J_{\text{KE}}$  leads to antiparallel spin ordering via cyanide covalent bond i.e. anti-ferromagnetic interaction  $J_{\text{AF}}$ . The  $J_{\text{PE}}$  leads to a parallel spin ordering that means ferromagnetic interaction  $J_{\text{F}}$ . This model has been already successfully tested on  $\text{TM}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$ , where  $\text{TM}^{2+}$  is  $3d$  ion, with the simplification that only the superexchange interactions between the nearest neighbour metal A and B ions have to be considered [2, 4]. Magnetic properties of mixed ferro-ferrimagnet  $(\text{Ni}_x\text{Mn}_{1-x})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  and pole inversion at the compensation temperature  $T_{\text{comp}}$  for different values of  $x$  were first reported in [5]. The possibility that the spontaneous magnetization might change sign at particular  $T_{\text{comp}}$  was envisaged by Néel in the classical theory of ferrimagnets [6].

Recently we reported on magnetic structure, magnetic properties and effect of pressure on magnetization in mixed ferro-ferrimagnet  $(\text{Ni}_x\text{Mn}_{1-x})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  in [7, 8]. In our paper we study magnetic properties of the  $(\text{Cu}_x\text{Mn}_{1-x})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  molecule-based magnets, where  $x = 0.0, 0.2, 0.25, 0.3, 0.35, 0.4, 0.6, 0.8$  and  $1.0$ . In this special case  $\text{Cr}^{\text{III}}$  in anion  $[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$  has  $(t_{2g})^3$  orbitals and there are 6 ferromagnetic and 9 antiferromagnetic pathways with  $(t_{2g})^3(e_g)^2$  orbitals of  $\text{Mn}^{2+}$  leading to overall  $J_{\text{AF}}$ . On the other hand,  $(t_{2g})^3$  orbitals of  $\text{Cr}^{\text{III}}$  have 3 ferromagnetic pathways with  $(e_g)^1$  orbitals of  $\text{Cu}^{2+}$  leading to overall  $J_{\text{F}}$ . Mn and Cu ions are both high spin with  $S_{\text{Mn}} = 5/2$  and  $S_{\text{Cu}} = 1/2$ . Cr ion is in low spin state with  $S_{\text{Cr}} = 3/2$ .

The compounds were prepared from an aqueous solution. Concentrated solutions of  $\text{K}_3[\text{Cr}(\text{CN})_6]$  have been added into the solutions containing  $\text{MnCl}_2$  and  $\text{CuCl}_2$  salts in molar ratios according to the desired compositions. In a few seconds, precipitates of the target compounds appeared. Prepared complexes have been filtrated and fully washed with distilled water. Expected crystal structure fcc space group  $Fm\bar{3}m$  was confirmed for all samples. Lattice parameters decrease nearly linearly with substitution of Cu for Mn:  $a = 10.51909$  nm,  $10.49812$  nm,  $10.50418$  nm,  $10.49833$  nm,  $10.4887$  nm,  $10.3851$  nm for  $x = 0.2, 0.25, 0.3, 0.35, 0.4$  and  $1.0$ , respectively. The lattice parameter  $a = 10.7538$  nm of  $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$  [2] does not fit to this linear dependence and is much higher. Number of water molecules  $n \approx 16$  was estimated from thermo-gravimetric measurements. Chemical structure was verified by infrared spectrometry.

## 2. Results and discussion

The typical temperature dependences of magnetization  $\mu(T)$  which were measured in zero field cooled (ZFC) and field cooled (FC) regimes are shown in

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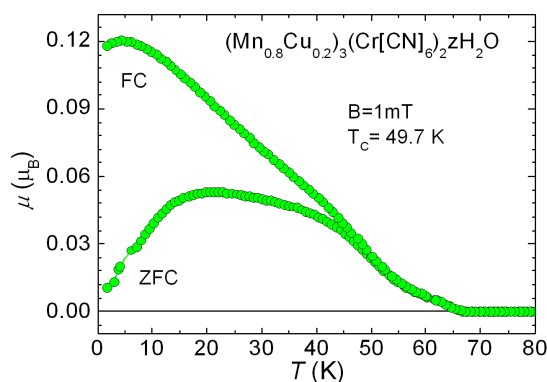


Fig. 1. Temperature dependence of magnetization measured in ZFC and FC regimes on the sample with  $x = 0.2$ .

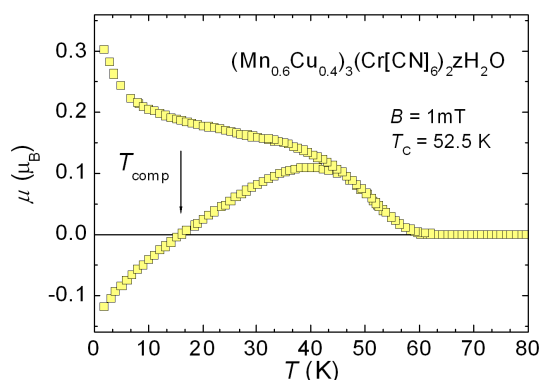


Fig. 2. Temperature dependence of magnetization measured in ZFC and FC regimes on the sample with  $x = 0.4$ . Arrow points on the compensation temperature.

Fig. 1 for a sample with the lowest value of saturated magnetization  $\mu_s$ . Very large hysteretic behaviour between ZFC and FC curves is a typical feature of the whole set of the samples. Magnetic susceptibility of  $(\text{Cu}_{0.2}\text{Mn}_{0.8})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  follows the Curie–Weiss law above 120 K with the effective magnetic moment  $\mu_{\text{eff}} = 685 \mu_B$  and the paramagnetic Curie temperature  $\theta = 40$  K. The positive value of  $\theta$  indicates that  $J_F$  is dominant in the compound which is the opposite situation with e.g.  $(\text{Ni}_{0.38}\text{Mn}_{0.62})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  mixed ferro-ferrimagnet system with dominant  $J_{\text{AF}}$  coupling. The Curie temperature of the investigated compound  $T_C = 49.7$  K, determined as inflection point in  $\mu(T)$  curve, is smaller than those of  $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  ( $T_C = 66$  K), additional substitution increases  $T_C$  reaching the value of about 60 K for  $\text{Cu}_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$ . The values of another magnetic characteristic quantities like  $\mu_{\text{eff}}$  and  $\theta$  decrease with substitution in comparison with both Mn- or Cu-parent compound. ZFC magne-

tization curve regime of  $(\text{Cu}_{0.4}\text{Mn}_{0.6})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  reaches zero value at  $T_{\text{comp}}$  (Fig. 2). The compensation temperature can be observed in ZFC curve because algebraic sum of  $\mu(T)$  or  $\text{Mn}^{2+}-\text{N}\equiv\text{C}-\text{Cr}^{\text{III}}$  subsystem and  $\text{Cr}^{\text{III}}-\text{C}\equiv\text{N}-\text{Cu}^{2+}$  subsystem is zero at  $T_{\text{comp}}$  [9].

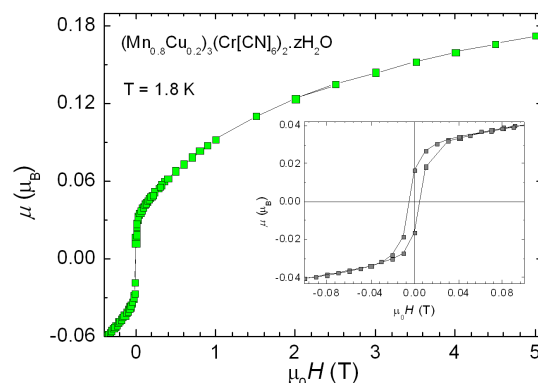


Fig. 3. Magnetization hysteresis loops of sample with  $x = 0.2$  measured at 1.8 K. The inset shows details of the magnetization curve at low magnetic fields.

In conclusion our magnetization measurements performed on the  $(\text{Cu}_x\text{Mn}_{1-x})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  molecule-based magnets indicate that this system behaves as mixed ferro-ferrimagnetic system and the compensation temperature can be observed. The dominant coupling of the system is  $J_F$  which is opposite coupling than was observed on  $(\text{Ni}_{0.38}\text{Mn}_{0.62})_3[\text{Cr}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  mixed ferro-ferrimagnetic compound.

#### Acknowledgments

This work was supported by the projects VEGA 2/0057/10 and SK-SI-0032-08.

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