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

Magnetic Properties of $(Cu_xMn_{1-x})_3[Cr(CN)_6]_2{\cdot}zH_2O$ Complexes

M. Vavra[a,b], M. Antoňák[a], Z. Jagličić[c], M. Mihalik[a,*], M. Mihalik[d], K. Csach[a] and M. Zentková[a]

[a]Institute of Experimental Physics, SAS, Watsonova 47, 040 01 Košice, Slovakia
[b]Institute of Chemistry, P.J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia
[c]Institute of Mathematics, Physics and Mechanics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia
[d]BENSC — Helmholtz-Zentrum, Glienicker Str. 100, 141 09 Berlin, Germany

Magnetization measurements were performed on the $(Cu_xMn_{1-x})_3[Cr(CN)_6]_2{\cdot}zH_2O$ 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 μ_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 $T_{comp} = 16$ 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^{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_{KE}) mediated directly via overlapping orbitals and potential exchange mechanism (J_{PE}) mediating interaction between orthogonal magnetic orbitals. The J_{KE} leads to antiparallel spin ordering via cyanide covalent bond i.e. antiferromagnetic interaction J_{AF}. The J_{PE} leads to a parallel spin ordering that means ferromagnetic interaction J_F. This model has been already successfully tested on $TM_3^{2+}[Cr^{III}(CN)_6]_2{\cdot}zH_2O$, where 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 $(Ni_xMn_{1-x})_3[Cr(CN)_6]_2{\cdot}zH_2O$ and pole inversion at the compensation temperature T_{comp} for different values of x were first reported in [5]. The possibility that the spontaneous magnetization might change sign at particular T_{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 $(Ni_xMn_{1-x})_3[Cr(CN)_6]_2{\cdot}zH_2O$ in [7, 8]. In our paper we study magnetic properties of the $(Cu_xMn_{1-x})_3[Cr(CN)_6]_2{\cdot}zH_2O$ 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 Cr^{III} in anion $[Cr^{III}(CN)_6]^{3-}$ has $(t_{2g})^3$ orbitals and there are 6 ferromagnetic and 9 antiferromagnetic pathways with $(t_{2g})^3(e_g)^2$ orbitals of Mn^{2+} leading to overall J_{AF}. On the other hand, $(t_{2g})^3$ orbitals of Cr^{III} have 3 ferromagnetic pathways with $(e_g)^1$ orbitals of Cu^{2+} leading to overall J_F. Mn and Cu ions are both high spin with $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$. Cr ion is in low spin state with $S_{Cr} = 3/2$.

The compounds were prepared from an aqueous solution. Concentrated solutions of $K_3[Cr(CN)_6]$ have been added into the solutions containing $MnCl_2$ and $CuCl_2$ 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-$3m$ 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 $Mn_3[Cr(CN)_6]_2{\cdot}nH_2O$ [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

* corresponding author; e-mail: mihalik@saske.sk

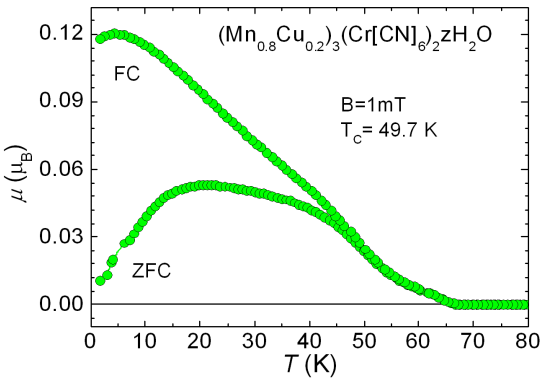

Fig. 1. Temperature dependence of magnetization measured in ZFC and FC regimes on the sample with $x = 0.2$.

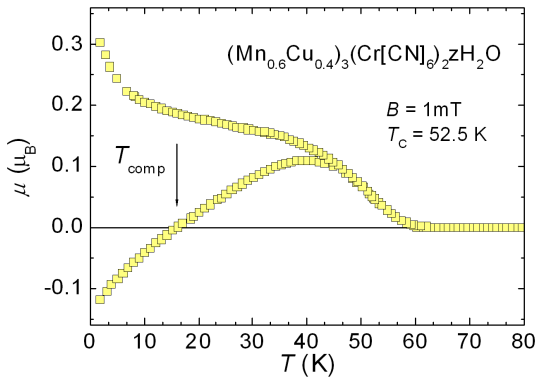

Fig. 2. Temperature dependence of magnetization measured in ZFC and FC regimes on the sample with $x = 0.4$. Arrow points on the compensation temperature.

Fig. 1 for a sample with the lowest value of saturated magnetization μ_s. Very large hysteretic behaviour between ZFC and FC curves is a typical feature of the whole set of the samples. Magnetic susceptibility of $(Cu_{0.2}Mn_{0.8})_3[Cr(CN)_6]_2 \cdot zH_2O$ 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 θ indicates that J_F is dominant in the compound which is the opposite situation with e.g. $(Ni_{0.38}Mn_{0.62})_3[Cr(CN)_6]_2 \cdot zH_2O$ mixed ferro-ferrimagnet system with dominant J_{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 $Mn_3[Cr(CN)_6]_2 \cdot zH_2O$ ($T_C = 66$ K), additional substitution increases T_C reaching the value of about 60 K for $Cu_3[Cr(CN)_6]_2 \cdot zH_2O$. The values of another magnetic characteristic quantities like μ_{eff} and θ decrease with substitution in comparison with both Mn- or Cu-parent compound. ZFC magnetization curve regime of $(Cu_{0.4}Mn_{0.6})_3[Cr(CN)_6]_2 \cdot zH_2O$ reaches zero value at T_{comp} (Fig. 2). The compensation temperature can be observed in ZFC curve because algebraic sum of $\mu(T)$ or Mn^{2+}–N≡C–Cr^{III} subsystem and Cr^{III}–C≡N–Cu^{2+} subsystem is zero at T_{comp} [9].

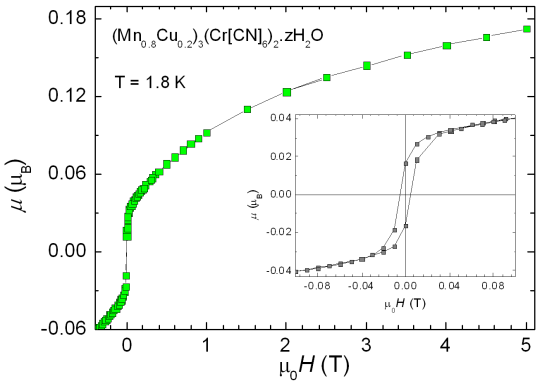

Fig. 3. Magnetization hysteresis loops of sample with $x = 0.2$ measured at 1.8 K. The inset shows details of the magnetization curve at low magnetic fields.

In conclusion our magnetization measurements performed on the $(Cu_xMn_{1-x})_3[Cr(CN)_6]_2 \cdot zH_2O$ 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 $(Ni_{0.38}Mn_{0.62})_3[Cr(CN)_6]_2 \cdot zH_2O$ mixed ferro-ferrimagnetic compound.

Acknowledgments

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

References

[1] D. Gatteschi, O. Kahn, J.S. Miller, F. Palacio, *Molecular Magnetic Materials*, *NATO ASI Series, Series E* Vol. 198, Kluwer, Dordrecht 1991.

[2] M. Verdaguer, G. Girolami, in: *Magnetism: Molecules to Materials V*, Eds. J.S. Miller, M. Drilon, Wiley-VCH Verlag GmbH& KGaA, Weinheim 2004.

[3] J.B. Goodenough, *Phys. Rev.* **100**, 564 (1959).

[4] M. Zentková, M. Mihalik, J. Kováč, A. Zentko, Z. Mitróová, V. Kavečanský, L.F. Kiss, 2006 *Phys. Status Solidi B* **243**, 272 (2006).

[5] Ohkoshi Shin-ichi, T. Iyoda, A. Fujishima, K. Hashimoto, *Phys. Rev. B* **56**, 11642 (1997).

[6] L. Néel, *Ann. Phys. (Leipzig)* **3**, 137 (1948).

[7] M. Mihalik, V. Kavečanský, S. Mataš, M. Zentková, O. Prokhenko, G. André, *J. Phys., Conf. Ser.* **200**, 022035 (2010).

[8] M. Zentková, M. Mihalik, Z. Arnold, J. Kamarád, *J. Phys., Conf. Ser.* **200**, 022074 (2010).

[9] O. Kahn, *Nature* **399**, 21 (1999).