Magnetic properties of $\text{TM}_3[\text{Cr(CN)}_6]_2 \cdot n\text{H}_2\text{O}$

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Magnetization measurements performed on Prussian blue analogs $\text{TM}^{2+}_3[\text{Cr}^{III}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ (TM = Cr, Mn, Fe, Co, Ni, Cu) confirmed the dual character of the exchange interaction (antiferromagnetic AFM and ferromagnetic FM) in this system. AFM interaction dominates for the Cr$^{2+}$ sample and with rising atomic number $Z$ the FM interaction becomes more important reaching pure FM character for the Cu$^{2+}$ sample.

1 Introduction

Recently, Prussian blue analogs have received increasing attention as molecule-based magnets [1, 2]. Prussian blue analogs build a large family of cubic systems $C_xA_y[B(\text{CN})_6]_z \cdot n\text{H}_2\text{O}$ where $A$ occupies all the summits and all the centers of the faces and the $[B(\text{CN})_6]$ are located at the octahedral sites. $C$ is a monovalent cation, which can be inserted into some of the tetrahedral sites of this cubic structure. One possible structure displays a $A:B = 3:2$ stoichiometry, with one third of $[B^{III}(\text{CN})_6]$ vacancies filled by water molecules; the $B$ coordination sphere is left unchanged but the mean coordination sphere of $A$ becomes $A(\text{NC})_4(\text{H}_2\text{O})_2$. The mean number of $B$ neighbors around $A$ is now four and the crystal structure is face-centered (fcc) [2]. The Prussian blue analogs usually present a cell parameter ranging from 10.0 to 10.9 Å [3]. This value corresponds to the $A$–$A$ ($B$–$B$) distances between two identical metallic ions in the network. To analyze the magnetic properties of Prussian blue analogs two simplifications can be made: (a) Only the superexchange interactions between the nearest-neighbor metal ions have to be considered [4]. (b) The character of superexchange interactions can be easily predicted from a simple orbital symmetry rule [5]. For example, when the magnetic orbital symmetries of the metal ions are the same, the superexchange interaction is antiferromagnetic ($J_{\text{AF}}$). Conversely, when their magnetic orbital symmetries are different, the super-exchange interaction is ferromagnetic ($J_F$). This simple model has been already tested on the $\text{TM}^{2+}_3[\text{Cr}^{III}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ system, $\text{TM}^{2+}$ is a 3d ion [2]. Pronounced correlations of the model with experimental data are found. On the other hand, all the experimental results can not be explained only by this model. One motivation to study this system is a search for a molecule-based magnet with Curie temperatures above room temperature. The highest Curie temperature, $T_C = 315$ K, has been achieved on a V$^{2+}$ sample [6]. Photomagnetic phenomena and magneto-optic phenomena motivated several studies [7, 8]. Moreover, novel types of magnets exhibiting two compensation temperatures are

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studied [9, 10]. In all these cases the knowledge of the basic magnetic properties is of high importance. Recently, we reported on the magnetic properties of vanadium hexacyanochromates [11, 12]. In this paper we present our study of magnetic properties of Prussian blue analogs TM$_2$[Cr(CN)$_6$]$_2$$\cdot$nH$_2$O (TM = Cr, Mn, Fe, Co, Ni, Cu). Our results are compared with the prediction of the simple model [2]. In addition we focused on a study of possible evidences of spin-glass-like or cluster-glass-like behavior in these compounds.

2 Experimental

The samples were synthesized by mixing a K$_3$[Cr(CN)$_6$] aqueous solution and TMCl$_2$ aqueous solution (except Fe$^{2+}$, where FeSO$_4$ was used). The diffraction pattern was taken using an X'PERT PRO (Panalytical) diffractometer (Cu Kα radiation). The crystal structure of the samples was refined by the Rietveld method using software package FullProf [13] on the basis of a structural model [14]. The crystal structure symmetry was confirmed to be cubic, space group Fm-3m (No 225). Refined values of lattice parameter are $a = 10.7540(1)$, $10.4905(3)$, $10.4341(3)$, $10.3851(2)$ Å, for TM = Mn, Co, Ni and Cu. The compounds are characterized by IR spectroscopy (Avatar 330). The number of water molecules in the crystal structure was determined from TG measurements (SETARAM TG/DTA 9L). Magnetic properties were studied in the temperature range $1.7 \leq T \leq 300$ K and in magnetic fields up to $\mu_0H = 5$ T using a MPMS (SQUID) magnetometer and $4 \leq T \leq 300$ K and in magnetic fields up to $\mu_0H = 6$ T using a VSM magnetometer.

3 Results and discussion

The onset of the ferri- or ferromagnetically ordered state is witnessed by observation of the steep increase in thermomagnetic curves upon cooling, as can be seen in Fig. 1. The Curie temperature $T_c$, determined as an inflection point of this increase, the minimum on the dM/dT plot measured at low magnetic field, varies from 19 K for Fe$^{2+}$ up to 220 K for Cr$^{2+}$ sample (see Fig. 2b). Values of all Curie temperatures are comparable with results already published in Ref. [2]. A characteristic feature of the whole series is the observation of the irreversibility between magnetization measured in the ZFC and FC regime with the temperature of irreversibility $T_{irr}$ (measured at 2 mT) slightly higher than $T_c$. The value of $T_{irr}$ weakly decreases with applied magnetic field. The exceptions are the Cr$^{2+}$ sample, where the huge decrease of $T_{irr}$ was observed (from $T_{irr} = 200$ K for $\mu_0H = 2$ mT to $T_{irr} = 110$ K for $\mu_0H = 15$ mT) (see Fig. 1) and the Cu$^{2+}$ sample (from $T_{irr} = 54$ K for $\mu_0H = 2$ mT to $T_{irr} = 37$ K for $\mu_0H = 7.5$ mT). The rounded maximum at the temperature $T_m$ was observed in all ZFC plots except of the Mn$^{2+}$ sample. Its position shifts with increasing magnetic fields (up to 15 mT) to the lower temperatures and for sufficiently high field (1 T) the maximum and the irreversible behavior vanishes completely. However, the position of $T_M$ is fixed for all applied magnetic fields (up to 15 mT) in the case of the Ni$^{2+}$ sample. Such behavior is frequently observed for ferri- or antiferromagnetic ordering with dominant antiferromagnetic (AFM) exchange interaction. On the other hand, in the case of Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$ samples the dominancy of ferromagnetic (FM) exchange interaction is expected and we have to consider another explanation, for instance, dual-exchange interaction or spin-glass-like behavior originating from structural disorder.

Magnetic susceptibility obeys the Curie–Weiss law on all tested samples at least 100 K above the phase transition. The Curie–Weiss law was not tested on the Cr$^{2+}$ sample, because the susceptibility data above $T_{nc} = 220$ K up to 300 K are still affected by magnetic short-range correlations. Typical $1/\chi(T)$ plots are displayed in the inset of Fig. 2 and the parameters obtained from the Curie–Weiss law are summarized in Fig. 4. In the case of Mn$^{2+}$ sample the modified Curie–Weiss law $\chi = \chi_0 + C(T - \theta)$, $\chi_0 = 8.4 \times 10^{-8}$ m$^3$/mol fits better the experimental data above 170 K. The effective magnetic moment $\mu_{eff}$ is, in the majority of cases, smaller than the saturated moment $\mu_s$ but both moments follow nearly the same dependence on atomic number Z as can be seen from Fig. 4a. The paramagnetic Curie temperature $\theta$ is negative for the Mn$^{2+}$ sample ($\theta = -5.7$ K) and positive for all remaining samples rising from $\theta = 24$ K for the Fe$^{2+}$ sample to $\theta = 90$ K for Cu$^{2+}$ sample (see Fig. 4b). The negative value of $\theta$ clearly
indicates AFM exchange interaction, but in ferrimagnets, with the same type of interaction, the value of \( \theta \) can be positive. There are indications that in \( \text{TM}_2\{\text{Cr(CN)}_6\}_{2n}\cdot n\text{H}_2\text{O} \) compounds the nature of the exchange pathway has dual character. The AFM interaction dominates for the \( \text{Cr}^{2+} \) sample, with increasing atomic number \( Z \) becomes weaker and the FM interaction dominates for the \( \text{Cu}^{2+} \) sample.

The typical curve of \( \chi T(T) \) shown in Fig. 2 again can indicate ferrimagnetic ordering. The value of \( \chi T \) is nearly constant or slightly increases on cooling.

Magnetization has a tendency to saturate very easy for all samples, as can be seen from Fig. 3a. The obtained magnetic moment can be compared with the theoretical one assuming two types of interaction AFM or FM between \( \text{TM}^{2+} \) ion and \( \text{Cr}^{III} \) ion and assuming that the Lande factor \( g = 2 \) for all samples. For \( \text{Cr}^{2+} \) and \( \text{Mn}^{2+} \) samples we expect AFM interaction. The theoretical value \( \mu_{\text{theor}} = 6\mu_0/\text{f.u.} \) (\( \text{Cr}^{2+} \) sample) is much higher than the experimental value of \( \mu_s = 1.7\mu_0/\text{f.u.} \) indicating a high tendency for compensation of spins in this sample; on the other hand \( \mu_{\text{theor}} = 9\mu_0/\text{f.u.} \) (\( \text{Mn}^{2+} \) sample) is more comparable with
\( \mu_s = 7.7 \mu_B/\text{f.u.} \). In the remaining samples \( \mu_s \) is better related to \( \mu_{\text{theor}} \) if FM interaction is assumed (\( \mu_{\text{theor}} = 18, 15, 12, 9 \mu_B/\text{f.u.} \) and \( \mu_s = 11.4, 11.5, 10.3, 8.8 \mu_B/\text{f.u.} \) for Fe, Co, Ni and Cu). These results suggest the dual character of the exchange interaction. The best agreement between theoretical prediction and experimental results was obtained on the Cu\textsuperscript{2+} sample indicating its ferromagnetic character.

Another characteristic feature of this system is the low value of coercive force \( \mu_0 H_C \), indicating soft magnetic behavior. Magnetization curves, measured at \( T = 4.2 \) K, display small hysteretic behavior with nearly zero values of remanent magnetization \( \mu_r \) and coercive force of \( \mu_0 H_C \approx 1 \) mT for the Mn and Ni samples, respectively, with rising values of these parameters for the remaining samples reaching the maximal value for the Co sample (\( \mu_r = 5.87 \mu_B/\text{f.u.} \) and \( \mu_0 H_C = 68 \) mT) as shown in Fig. 3b.

### 4 Summary

Our results are summarized in Fig. 4. Starting from the Cr\textsuperscript{2+} sample magnetic moment \( \mu_s \) and \( \mu_{\text{eff}} \) first increase with increasing \( Z \), reaches a maximum for the Fe\textsuperscript{2+} and Co\textsuperscript{2+} samples and then decreases (see Fig. 4a). Characteristic temperatures \( T_C \), \( T_{\text{irr}} \) (measured at 2 mT) and \( |\theta| \) first decrease with increasing \( Z \), reaches a minimum for the Fe\textsuperscript{2+} and Co\textsuperscript{2+} samples and then increases (see Fig. 4b). AFM interaction dominated for the Cr\textsuperscript{2+} sample leads to high value of \( T_C \) and a small value of \( \mu_s \). The increasing influence of FM interaction with increasing value of \( Z \) reduces \( T_C \), and increases the magnetic moment. FM interaction starts to be critical for the Ni\textsuperscript{2+} sample and is typical for the Cu\textsuperscript{2+} sample.

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**References**


