Effect of Pressure on Magnetic Properties of Hexacyanochromates

Z. Mitróová, S. Maťaš, M. Mihalik, M. Zentková

Institute of Experimental Physics, Slovak Academy of Sciences
Watsonova 47, 040 01 Košice, Slovak Republic

Z. Arnold and J. Kamarád

Institute of Physics of the AS CR, v.v.i.
Na Slovance 2, 182 21 Prague 8, Czech Republic

We present the study of pressure effect on magnetic properties of $TM_3^{2+}[Cr^{III}(CN)_6]_2 \cdot nH_2O$ ferrimagnets and ferromagnets (TM = Cr and Co) under pressures up to 0.9 GPa. Applied pressure strengthens super--exchange interaction in Cr^{2+}-prussian blue analogues with dominant antiferromagnetic interaction J_{AF} leading to increase in the Curie temperature T_C ($\Delta T_c/\Delta p = 29.0$ K/GPa) and reduces T_C of Co^{2+}-prussian blue analogues with dominant ferromagnetic interaction J_F ($\Delta T_c/\Delta p = -1.8$ K/GPa). The rise of J_{AF} interaction is attributed to the enhanced value of the single electron overlapping integral S. On the other hand, the applied pressure slightly affects bonding angles between magnetic ions mediated by the cyano-bridge and reduces the strength of magnetic coupling. Changes of the magnetization curve with pressure can be attributed to changes of magnetic anisotropy. The reduction of magnetization with pressure observed on Cr^{2+}-prussian blue analogues can be explained by pressure induced transition from Cr^{2+} high spin state to Cr^{2+} low spin state. All pressure induced changes are reversible.

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1. Introduction

Prussian blue analogues (PBA) form a large family of cubic systems with face-centered (fcc) crystal structure and one of the possible stoichiometry is $A_3^{2+}[B^{III}(CN)_6]_2^{3-} \cdot nH_2O$ [1–3]. Magnetic properties of PBA can be analyzed within two simplifications: (i) only the super-exchange interaction between the nearest neighbor metal A^{2+} and B^{III} ($A^{2+}-N \equiv C-B^{III}$) ions have to be considered; (ii) if the magnetic orbital symmetries of the metal ions are the same,

the super-exchange interaction is antiferromagnetic (J_{AF}); conversely, when their magnetic orbital symmetries are different, the super-exchange interaction is ferromagnetic (J_{F}) [1–3]. The B^{III} ion, surrounded by the carbon atoms of six cyanide ligands, experiences a large ligand field. As a result, all known $[B^{\mathrm{III}}(\mathrm{CN})_6]$ units are invariably low-spin and have electrons only in the $t_{2\mathrm{g}}$ orbitals. The A^{2+} ion, surrounded by nitrogen atoms of cyanide ligands or oxygen from water molecules, is in a weak ligand field and is almost always high-spin. The Cr^{2+} ion is an exception having high spin $S = 2$ with magnetic orbitals $(t_{2\mathrm{g}})^3(e_{\mathrm{g}})^1$ and low spin $S = 1$ with magnetic orbitals $(t_{2\mathrm{g}})^2$ as well [4]. In our recent paper [5] we presented results of the pressure effect on magnetic properties of $\mathrm{TM}_3^{2+}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6]_2 \cdot n\mathrm{H}_2\mathrm{O}$, where $\mathrm{TM}^{2+} = \mathrm{Mn}^{2+}$ and Ni^{2+}. In this work we extended our study on PBA with $\mathrm{TM}^{2+} = \mathrm{Cr}^{2+}$ and Co^{2+}.

2. Experimental

Samples of $\mathrm{TM}_3^{2+}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6]_2 \cdot n\mathrm{H}_2\mathrm{O}$, where $\mathrm{TM} = \mathrm{Cr}$ or Co, were synthesized by mixing $\mathrm{K}_3[\mathrm{Cr}(\mathrm{CN})_6]$ and TMCl_2 aqueous solutions. The crystal structure symmetry was confirmed as cubic, space group $Fm\text{-}3m$ (No. 225). The refined value of the lattice parameter for $\mathrm{Cr}_3[\mathrm{Cr}(\mathrm{CN})_6]_2 \cdot 2\mathrm{H}_2\mathrm{O}$ is $a = 1.03805(9)$ nm and $a = 1.04905(3)$ nm for $\mathrm{Co}_3[\mathrm{Cr}(\mathrm{CN})_6]_2 \cdot 10\mathrm{H}_2\mathrm{O}$. The number of water molecules in the crystal structure was determined from thermo-gravimetric measurements. Magnetizations were measured in the temperature range $8\ \mathrm{K} \le T \le 100\ \mathrm{K}$ and in magnetic fields up to $\mu_0 H = 5$ T using a SQUID magnetometer (MPMS). Pressure was generated by a hydrostatic CuBe pressure cell filled with a mixture of mineral oils serving as the pressure transmitting medium and operating up to 1.2 GPa. The pressure experiment was performed by the same way as it is described in [5]. Pressure induced changes of the saturated magnetization μ_s and the Curie temperature T_C are reversible.

3. Results

The transition to a magnetically ordered state is accompanied by a steep increase in $M(T)$ (see Fig. 1). The Curie temperature T_C is defined as the inflection point of the $M(T)$ curve in this region. The applied pressure shifts T_C of Cr^{2+}–$\mathrm{Cr}^{\mathrm{III}}$–PBA to higher temperatures almost linearly in this range of applied pressures (Fig. 1a). The estimated positive coefficient $\Delta T_\mathrm{C}/\Delta p = 29$ K/GPa is the highest positive change of T_C with pressure which has so far been published for any PBA. From the Hückel calculations [2] follows that the antiferromagnetic contribution to the coupling J is given approximately by the expression $2S(\Delta^2 - \delta^2)^{1/2}$, where δ is the energy gap between (unmixed) $\boldsymbol{a}$ and $\boldsymbol{b}$ orbitals, Δ is the energy gap between the molecular orbitals built from them, and S is the monoelectronic overlap integral between $\boldsymbol{a}$ and $\boldsymbol{b}$. The applied pressure reduces the length of exchange path $\mathrm{Cr}^{2+}-\mathrm{N} \equiv \mathrm{C}-\mathrm{Cr}^{\mathrm{III}}$ and increases overlap integral S. The applied pressure can
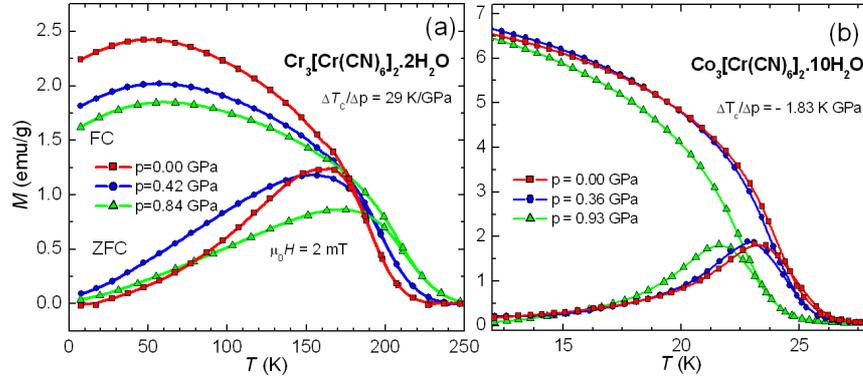
Fig. 1. Magnetization $M(T)$ measured under different pressures in ZFC and FC regimes in magnetic field $\mu_0 H = 2$ mT for (a) $Cr^{2+}-Cr^{III}-PBA$ and (b) $Co^{2+}-Cr^{III}-PBA$.

increase Δ leading to an increase in both terms $(\Delta - \delta)$, $(\Delta + \delta)$ and this way leads to strengthening of the antiferromagnetic coupling.

The applied pressure shifts T_C of $Co^{2+}-Cr^{III}-PBA$ to lower temperatures in this range of applied pressures (Fig. 1b) with the estimated negative coefficient $\Delta T_C / \Delta p = -1.8$ K/GPa. In the case of t_{2g} and e_g orbitals the overlap is principally zero and J_F is not affected by pressure. The applied pressure can slightly affect bonding angles between magnetic ions mediated by the cyano-bridge and this can result in reduction of T_C.

Difference between $M(T)$ measured in zero field cooling (ZFC) and field cooling (FC) regime indicates region of irreversible behavior of magnetization processes (Fig. 1a and b). The irreversibility in ZFC and FC magnetization together with small maximum below T_C is usually associated with freezing temperature T_f of cluster glass system which is frequently observed in PBA. The applied pressure increases the difference between magnetization measured in ZFC and FC measurements for $Cr^{2+}-Cr^{III}-PBA$. Reduced value of magnetization $M(T)$ in ZFC regime indicates a change in ligand field leading to change of magnetocrystalline anisotropy.

The magnetic isotherms of $Cr^{2+}-Cr^{III}-PBA$ and $Co^{2+}-Cr^{III}-PBA$ measured under different pressures are shown in Fig. 2. Magnetization increases at first very steep, at very low field starts to saturate and above $\mu_0 H = 1$ T the magnetization increases almost linearly with magnetic field but it is not completely saturated at $\mu_0 H = 5$ T. The applied pressure reduces saturated magnetization of $Cr^{2+}-Cr^{III}-PBA$ (Fig. 2a). The Cr^{III} in anion $[Cr^{III}(CN)_6]^{3-}$ is low spin and has only $(t_{2g})^3$ orbital and the spin $S = 3/2$. On the other hand, we can assume for cation Cr^{2+} two possibilities: at first Cr^{2+} is high spin that means $S = 2$ and magnetic orbitals are $(t_{2g})^3 (e_g)^1$ leading to 3 F and 9 AF pathways, or the second possibility when Cr^{2+} is low spin $S = 1$ and magnetic orbitals are $(t_{2g})^2$ leading to 6 AF pathways [4]. In the case that all Cr^{2+} are high spin, the expected theoretical value
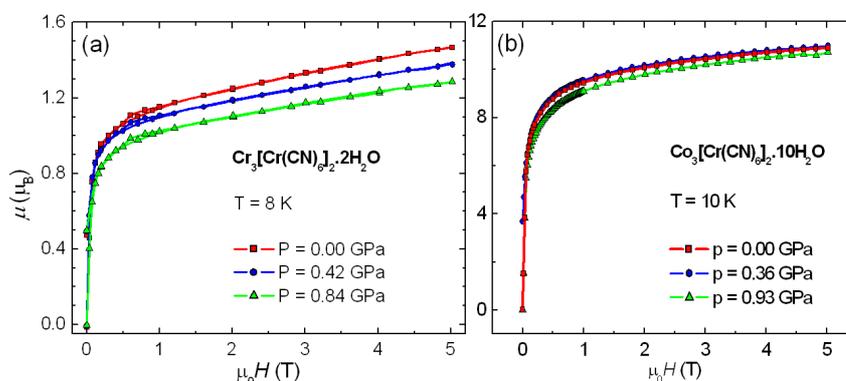
Fig. 2.   Magnetization $\mu(\mu_0 H)$ measured at two temperatures under different pressures:
(a) Cr^{2+}–Cr^{III}–PBA and (b) Co^{2+}–Cr^{III}–PBA.

of spontaneous magnetization $\mu_s = g[3S(Cr^{2+}) - 2S(Cr^{III})] = 6\mu_B$; $g = 2$ is the
Landé factor. The experimentally determined value $\mu_s(\exp) = 1.73\mu_B$ [4] is much
smaller than the theoretical one indicating that a part of Cr^{2+} is low spin $(S = 1)$
yielding total compensation of spins $\mu_s = 0\mu_B$. It seems that only approximately
30% of Cr^{2+} is high spin. The applied pressure $p = 0.84$ GPa induces another
high spin–low spin transition approximately 4.5% of high spin Cr^{2+}.

Magnetization of Co^{2+}–Cr^{III}–PBA is reduced only slightly. We suppose
that the applied pressure does not change spontaneous magnetization, and only
the magnetization process is significantly affected even at low temperatures. The
applied pressure increases the degree of deformation in the crystal structure, which
leads to mis-orientation of magnetic moments placed on magnetic ions and to
reduction of saturated magnetization.

Acknowledgments

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