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Effect of pressure on the magnetic properties of $\text{TM}_3[\text{Cr}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$

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Abstract

We present the results of magnetization and AC susceptibility measurements performed on ferrimagnetic $\text{Mn}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ and ferromagnetic $\text{Ni}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ systems under pressures up to 0.9 GPa in a commercial SQUID magnetometer. The magnetization process is affected by pressure: magnetization saturates at higher magnetic field, saturated magnetization μ_s of $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2$ is reduced and almost unaffected for $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2$ at low temperatures. The Curie temperature T_C of $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2$ increases with the applied pressure, $\Delta T_C/\Delta p = 25.5 \text{ K GPa}^{-1}$, due to a strengthened super-exchange antiferromagnetic interaction J_{AF} , but it is not affected significantly in the case of $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2$ with a dominant ferromagnetic J_{F} super-exchange interaction. The increase in the J_{AF} interaction is attributed to the enhanced value of the single electron overlapping integral S and the energy gap Δ of the mixed molecular orbitals t_{2g} (Mn^{2+}) and t_{2g} (Cr^{III}) induced by pressure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Prussian blue analogues (PBA) are the subject of increasing interest mostly because of the possibility of producing molecule-based magnets working at room temperature and because of the sensitivity of their magnetic properties to different types of external stimuli [1]. PBA form a large family of cubic systems with face-centred (fcc) crystal structure. One of the possible stoichiometries is $\text{A}_3[\text{B}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ where A occupies all the summits and all the centres of the faces and the $[\text{B}(\text{CN})_6]$ are located at the octahedral sites. One-third of $[\text{B}(\text{CN})_6]$

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vacancies are filled by water molecules; the B coordination sphere is left unchanged but the mean coordination sphere of A becomes $A(\text{NC})_4(\text{H}_2\text{O})_2$ [1–3]. The magnetic coupling in these systems is determined by super-exchange interaction between metal ions A^{2+} and B^{III} mediated through a three-dimensional network of C–N bridges, resulting in 3D magnetic ordering with transition temperatures T_C up to 376 K [2] depending on the nature of the metal ions. The magnetic properties of PBA can be analysed within two simplifications: (i) only the super-exchange interactions between the nearest neighbour metal A^{2+} and B^{III} (A^{2+} –N≡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 $[B^{\text{III}}(\text{CN})_6]$ units are invariably low-spin and have electrons only in the t_{2g} 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. This simple model has already been tested on the $\text{TM}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 15\text{H}_2\text{O}$ system, TM^{2+} is a 3d ion [1–4]. Cr^{III} in the anion $[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$ has only $(t_{2g})^3$ orbitals and there are six ferromagnetic (F) and nine antiferromagnetic (AF) pathways with $(t_{2g})^3(e_g)^2$ orbitals of Mn^{2+} leading to overall J_{AF} interaction. On the other hand, the $(t_{2g})^3$ orbitals of Cr^{III} have six F pathways with $(e_g)^2$ orbitals of Ni^{2+} leading to overall J_{F} interaction. Measurements of magnetic susceptibility [4] indicate a ferrimagnetic ordering below $T_C \sim 65$ K for the Mn sample with $\mu_{\text{eff}} = 10.48 \mu_B$ and $\theta = -39.5$ K. The magnetic moment μ_s saturates to a value of $8 \mu_B/\text{f.u.}$ at $T = 2$ K and $\mu_0 H = 5$ T. The Ni sample orders ferromagnetically below $T_C \sim 56$ K, $\mu_{\text{eff}} = 8.6 \mu_B$, $\theta = 72$ K. The magnetic moment saturates to a higher value of $\mu_s = 10.3 \mu_B/\text{f.u.}$ at $T = 2$ K and $\mu_0 H = 5$ T [4].

The pressure effect has recently been studied on 3D and layered cyano-bridged compounds. In the case of layered materials magnetic exchange interaction usually dominates within the layer and dipolar interaction takes place between layers. Dipolar energy is expected to exceed the exchange energy for distances larger than 10 \AA and to be several orders of magnitude larger than the exchange energy above 20 \AA . It has been shown for the layered hybrid compounds $\text{Cu}_2(\text{OH})_3(n\text{-C}_m\text{H}_{2m+1}\text{CO}_2) \cdot z\text{H}_2\text{O}$ that the distance between magnetic copper(II) layers, up to 4.07 nm, is not significantly modified by pressure up to 1 GPa and that T_C decreases linearly with pressure ($\Delta T_C/\Delta p = -3.4$ or -3.2 K GPa^{-1}). The decrease of T_C under pressure is shown to be mainly driven by the decrease of in-plane interactions, which can be caused by small variations of the Cu–O–Cu bond angles within the layer [9]. Similarly, measurements of magnetization and AC susceptibility performed under high pressure on polycrystalline layered copper octacyanotungstate (tetrenH₅)_{0.8}{Cu₄^{II}[W^V(CN)₈]₄}·7.2H₂O revealed a decrease of T_C with a pressure coefficient $\Delta T_C/\Delta p = -7.2 \text{ K GPa}^{-1}$. The pressure-induced reduction of the Curie temperature, as well as reduction of the coercive field and remanent magnetization, can be ascribed to the decrease of the intra-layer exchange interaction [6].

One of the most studied subjects in molecule-based magnetism is the photo-induced magnetization (PIM) effect [7]. PIM was observed for the first time in a cobalt–iron PBA and is explained by the presence of diamagnetic low-spin Co^{3+} – Fe^{II} pairs and a photo-induced electron transfer from Fe^{II} to Co^{3+} through the cyanide bridge to produce high-spin Co^{2+} –low-spin Fe^{III} magnetic pairs. A pressure-induced electron transfer in $\text{Co}^{2+}(S = 3/2)$ – $\text{Fe}^{\text{III}}(S = 1/2) \rightarrow \text{Co}^{3+}(S = 0)$ – $\text{Fe}^{\text{II}}(S = 0)$ was found on three cobalt–iron PBA and similarities with photoinduced electron transfer were discussed [8]. The PIM effect and pressure effect on structural properties were investigated for $\text{RbMn}[\text{Fe}(\text{CN})_6]$. Hydrostatic pressure up to about 2 GPa changes $\text{RbMn}[\text{Fe}(\text{CN})_6]$ from the tetragonal phase to a metastable state with different

crystal symmetry. The origin of the PIM effect can be explained by comparison of the photo-induced process with the pressure-induced process [5].

In several cases the Curie temperature increases under pressure and in this sense pressure experiments can tune T_C of the high- T_C molecule-based magnet. The increase in T_C of the bimetallic ferrimagnet $[\text{Mn}(\text{en})]_3[\text{Cr}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$ (monoclinic system, space group $C2/c$) from $T_C = 69$ K at ambient pressure to $T_C = 130$ K at $p = 4.7$ GPa was observed by measurements in a diamond anvil cell [10]. The observed gradual increase of the Curie temperature with pressure from $T_C = 29$ to 40 K at $p = 1$ GPa on a Mn-based Prussian blue ferrimagnet, $\text{Mn}_3^{2+}[\text{Mn}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O} \cdot 1.7(\text{CH}_3\text{OH})$, was semi-quantitatively interpreted in terms of the shrinkage of the $\text{Mn}^{\text{III}}\text{--CN--Mn}^{2+}$ super-exchange pathway [11].

Depending on the investigated cyano-bridged compound, application of high pressure changes the crystal structure, induces electron transfer, magnetic pole inversion and antiferromagnetic crossover [12] or affects magnetic interactions. In the present paper we study the pressure effect on the magnetic properties of ferrimagnetic $\text{Mn}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ and ferromagnetic $\text{Ni}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ compounds with almost the same Curie temperatures under pressures up to 0.9 GPa.

2. Samples and experiment

Samples of $\text{TM}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$, where $\text{TM} = \text{Mn}$ or Ni , were synthesized by mixing $\text{K}_3[\text{Cr}(\text{CN})_6]$ and TMCl_2 aqueous solutions. The x-ray powder diffraction pattern was taken using a HZG 4/A diffractometer (Co $K\alpha$ radiation, $\lambda = 1.7902$ Å) in the angular range of $10^\circ\text{--}100^\circ$ for 2θ (scan step size 0.02, time per step 20 s). The crystal structure of the samples was refined by the Rietveld method using the software package FullProf [13] on the basis of a structural model [14]. The crystal structure symmetry was confirmed as cubic, space group $Fm\bar{3}m$ (no 225). The refined value of the lattice parameter for $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ is $a = 10.75404(6)$ Å, and the x-ray diffraction pattern together with graphic outputs of the refinement process are displayed in figure 1. The refined value of the lattice parameter for $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ obtained by the same procedure is $a = 10.4341(3)$ Å. The crystal structure is displayed in figure 2 according to results published in [14]. The number of water molecules in the crystal structure was determined from thermogravimetric measurements (SETARAM TG/DTA 9L). Magnetization and AC susceptibility were studied in the temperature range 4.2 K $\leq T \leq 100$ 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. Actual pressure was determined from the pressure dependence $T_C(p)$ of the superconducting transition of the high purity lead ($T_C = 7.19$ K at ambient pressure). The pressure in the cell increases with increasing temperature in a nonlinear way [15], but this increase is comparable with the accuracy of the pressure determination, i.e. $\Delta p = 0.03$ GPa in the measured temperature range, and can be neglected. Powder samples with a mass of about 5 mg each were placed into a cylindrical holder 5 mm long and with a diameter of 2 mm. The pressure was always applied at room temperature. The experiment started with the highest pressure, which was then gradually decreased in steps. There was no difference between the saturated magnetization μ_s and the Curie temperature T_C determined at the ambient pressure before and after the pressure experiment.

3. Results and discussion

The magnetic isotherms of $\text{Mn}^{2+}\text{--Cr}^{\text{III}}\text{--PBA}$ measured for different pressures at two temperatures (8 and 50 K) are shown in figure 3. Magnetization saturates in very low magnetic

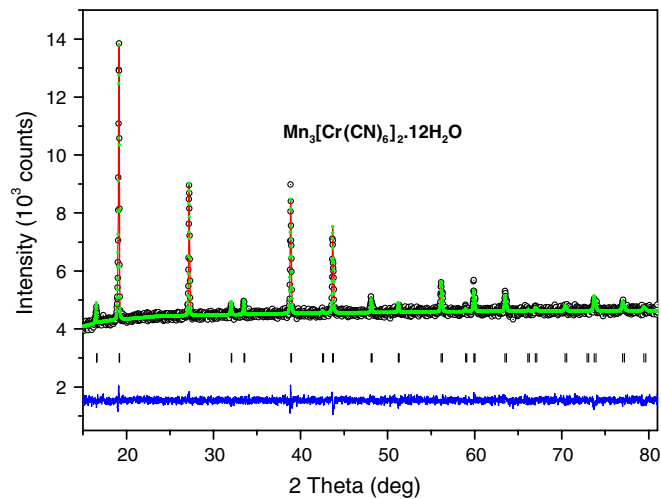


Figure 1. X-ray powder diffraction pattern of $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$. Experimentally measured intensities are indicated by circles and the calculated one by the line which overlays them. The positions of all possible Bragg reflections are marked by the vertical marks in the middle and the lower curve shows the difference between the observed and calculated intensities. Reliability factors of the refinement procedure for points with Bragg contributions are $R_p = 0.0127$, $R_{wp} = 0.0162$ and $\chi^2 = 1.23$.

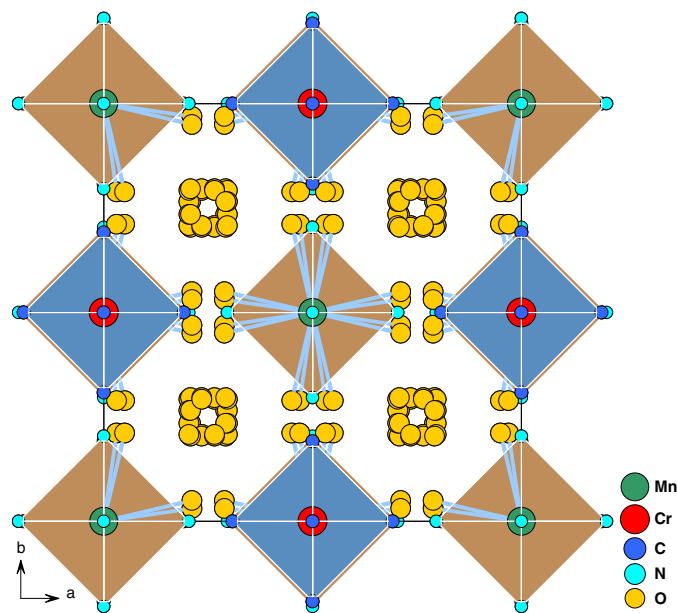


Figure 2. Crystal structure of $\text{Mn}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ plotted according to [14].

fields at low temperatures, and above $\mu_0 H = 200$ mT is almost independent of the rising magnetic field. The remanent magnetization μ_r and coercive field H_C for this material are close to zero [4]. As can be seen from figure 3(a), the magnetic isotherms change their shape with the applied pressure; magnetization saturates at higher magnetic field under pressure, but saturated

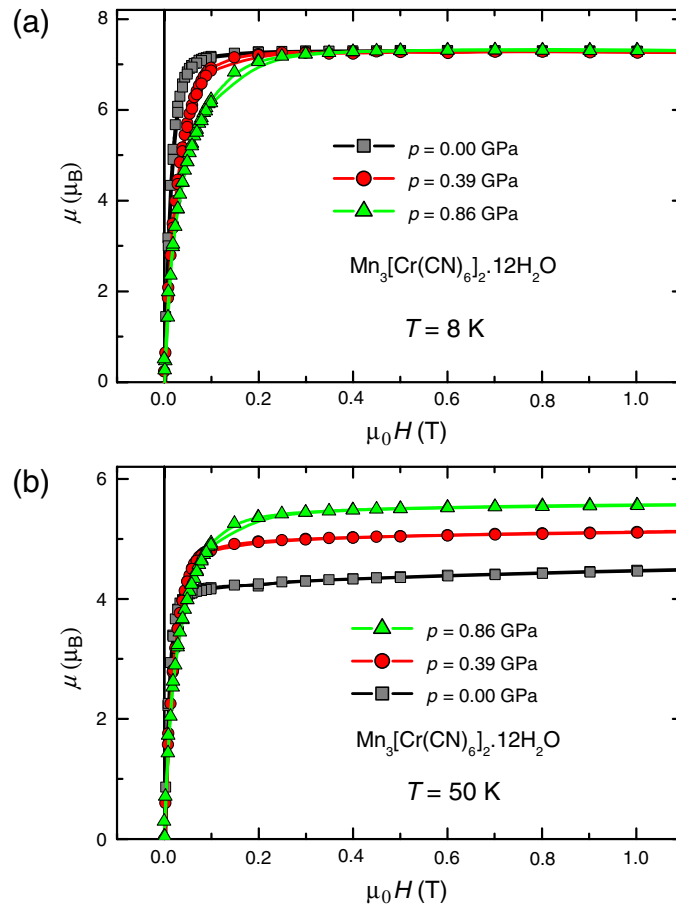


Figure 3. Magnetization $\mu(\mu_0 H)$ measured at two temperatures under different pressures. Below $T = 8 \text{ K}$ low field magnetization data are affected by the superconducting state of the Pb pressure sensor.

magnetization μ_s , μ_r , and H_C are not significantly affected by pressure at low temperatures. The applied pressure can induce effective barriers for domain-wall motion, and they move less freely in the irreversible part of the hysteretic loop, which results in a saturation of the magnetization at higher field. Another explanation for the behaviour observed in figure 3(a) is based on the change of magneto-crystalline anisotropy induced by pressure. The shape of the magnetic isotherms measured under pressure is reminiscent of magnetic isotherms measured along the hard magnetization axis. Both magnetic ions are placed in octahedral positions in the crystal structure. The alignment of magnetic moments is expected along the axes of the octahedrons. In the real crystal structure the octahedrons are tilted [1, 2]. The applied pressure can increase the degree of tilting and cause deformation of the octahedrons, both of which lead to change in magnetic anisotropy and reduction in the value of the magnetic moment. The effect of pressure on magnetic isotherms is different at higher temperatures (see figure 3(b)). Coming closer to the magnetic phase transition T_C the value of magnetization rises significantly with pressure. We expect that the value of the applied pressure is not sufficiently high to change the value of spontaneous magnetization or the value of the magnetic moment (spin) on the magnetic ion. The applied pressure increases the strength of magnetic interaction in the system,

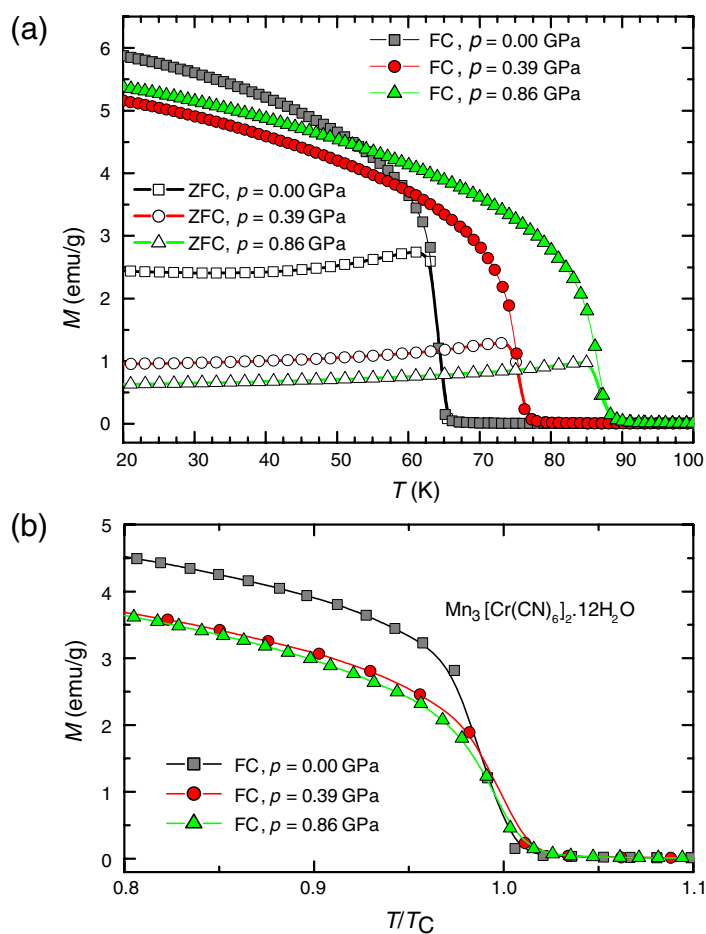


Figure 4. Magnetization $M(T)$ measured under different pressures: (a) in ZFC and FC regimes in the magnetic field $\mu_0 H = 1$ mT; (b) in the FC regime plotted at reduced temperature.

as indicating by the increase in T_C (see figure 4). The effect of pressure on the magnetization curve caused by the change in magneto-crystalline anisotropy is now masked by the effect of stronger magnetic coupling. Figure 4 illustrates the different behaviour of $M(T)$ for different magnetic couplings, e.g. at about $T = 70$ K the sample is in a paramagnetic state with the value of M close to zero at $p = 0.00$ GPa, but at $p = 0.39$ GPa the value of magnetization M is much higher, though still smaller than at $p = 0.86$ GPa. The pressure induced effect of magnetic hardening can be seen from figure 4(b), where FC curves are plotted at reduced temperature (T/T_C).

The transition to a magnetically ordered state is accompanied by a steep increase in $M(T)$ (see figure 4). 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 to higher temperatures almost linear in this range of applied pressures. The estimated positive coefficient $\Delta T_C/\Delta p = 25.5$ K GPa $^{-1}$ is the highest positive change of T_C with pressure which has so far been published for any PBA. Positive pressure coefficients $\Delta T_C/\Delta p \approx 14$ K GPa $^{-1}$ and $\Delta T_C/\Delta p \approx 11$ K GPa $^{-1}$ were recently reported for $[\text{Mn}(\text{en})_3][\text{Cr}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$ [10] and for

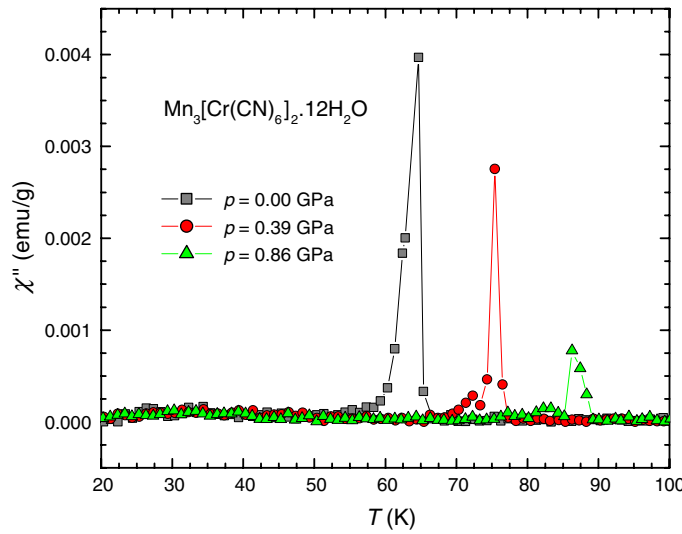


Figure 5. AC susceptibility $\chi''(T)$ measured under different pressures.

$\text{Mn}_3^{2+}[\text{Mn}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O} \cdot 1.7(\text{CH}_3\text{OH})$ [11] Mn-based PBA ferrimagnets, respectively. The characteristic feature of many PBA, i.e. a hysteretic behaviour between zero-field-cooled (ZFC) and field-cooled (FC) magnetization in low magnetic fields, was observed on $\text{Mn}^{2+}\text{-Cr}^{\text{III}}\text{-PBA}$ (see figure 4). Magnetization curves measured in ZFC and FC regimes are identical above the Curie temperature and with decreasing temperature they start to differ at the bifurcation temperature T_b . The difference between $M(T)$ measured in ZFC and FC regimes indicates a region of irreversible behaviour of magnetization processes. The irreversibility in ZFC and FC magnetization together with a small maximum below T_C is usually associated with freezing temperature T_f of the cluster-glass system which is frequently observed in PBA. The applied pressure increases the difference between magnetization measured in ZFC and FC measurements. The reduced value of magnetization $M(T)$ in the ZFC regime can again indicate a change in magneto-crystalline anisotropy induced by pressure. One can assume that the applied pressure makes the cluster-glass behaviour more pronounced.

Results for the pressure effect on AC in-phase susceptibility $\chi'(T)$, which was measured in a zero DC magnetic field, and modulation with the amplitude of 3 Oe and frequency $f = 0.4$ Hz, are similar to results of the $M(T)$ measurements under pressure in the ZFC regime (the applied pressure increases T_C and reduces the value of $\chi'(T)$), so we do not show this dependence in our paper. The characteristic feature of AC-out phase susceptibility $\chi''(T)$ is a sharp maximum at about T_C , indicating energy-dissipative processes accompanied by the creation of a magnetically ordered state (see figure 5). The maximum (T_C) is gradually shifted to higher temperatures with applied pressure, indicating the increase of T_C . The rate of increase of T_C with pressure, determined from a steep increase of $\chi'(T)$ or as a maximum in $\chi''(T)$, is comparable with $\Delta T_C/\Delta p = 25.5 \text{ K GPa}^{-1}$ determined from $M(T)$ measurements.

Mn^{2+} has five unpaired d-electrons ($t_{2g})^3(e_g)^2$ with $S = 5/2$ and Cr^{III} has three d-electrons ($t_{2g})^3$ with $S = 3/2$ in the $\text{Mn}^{2+}\text{-Cr}^{\text{III}}\text{-PBA}$. In the ligand-field model [2] each t_{2g} orbital (**a**) of Mn^{2+} can find a t_{2g} orbital (**b**) in Cr^{III} with which it can strongly interact within a three-dimensional network. The super-exchange interaction of this pair will be antiferromagnetic. From the extended Hückel calculations performed in [2] it follows that the antiferromagnetic contribution to the coupling J is given approximately by the expression $2S(\Delta^2 - \delta^2)^{1/2}$, where

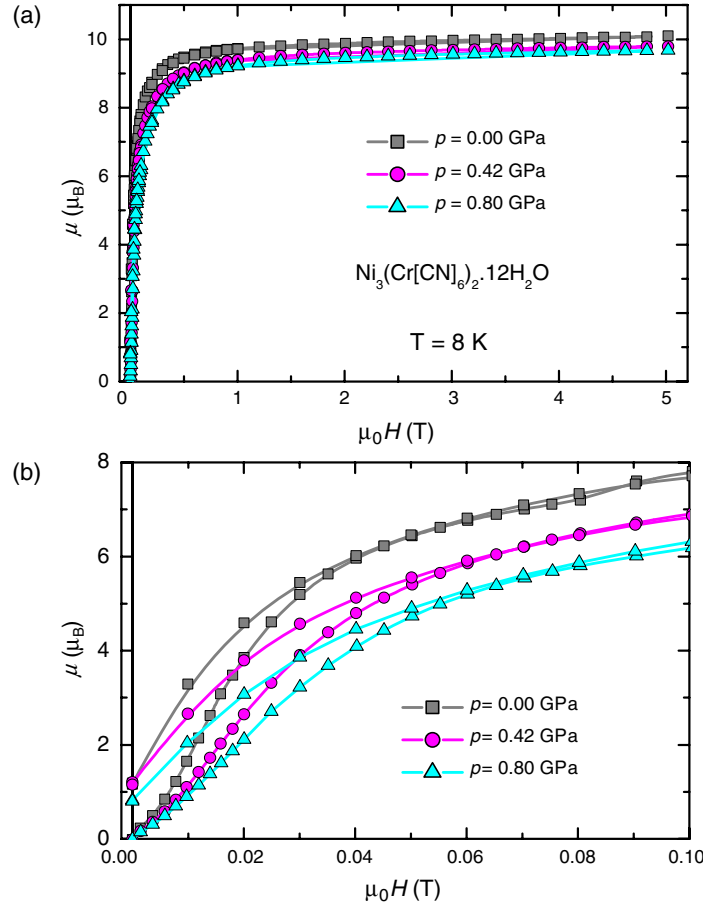


Figure 6. Magnetization $\mu(\mu_0H)$ measured under different pressures (a); and the detail of the same measurements in low magnetic fields (b). The lower curve represents measurements of initial magnetization.

δ is the energy gap between the (unmixed) **a** and **b** orbitals, Δ is the energy gap between the molecular orbitals formed by them, and S is the monoelectronic overlap integral between **a** and **b**. The antiferromagnetic term can be rewritten as $(\Delta^2 - \delta^2) = (\Delta - \delta)(\Delta + \delta)$; the strength of the interaction is gauged by the term $(\Delta - \delta)$ and the stabilization of charge-transfer states in which an electron is transferred from one magnetic orbital to the other is gauged by the term $\Delta + \delta$. The applied pressure reduces the volume of the unit cell and increases the value of overlap integral S . The increase of T_C in $\text{Mn}^{2+}\text{-Mn}^{\text{III}}\text{-PBA}$ [11] was attributed to an increase in the overlap integrals between $d_\pi(\text{Mn}^{\text{III}})$ and $\pi^*(\text{CN}^-)$ and between $d_\pi(\text{Mn}^{2+})$ and $\pi^*(\text{CN}^-)$ [11]. The applied pressure can increase Δ leading to an increase in both terms $(\Delta - \delta)$, $(\Delta + \delta)$, and in this way it leads to strengthening the antiferromagnetic coupling. The term $(\Delta^2 - \delta^2)$ was calculated for a number of TM^{2+} and TM^{III} with the assumption that the distance between magnetic ions is the same [2]; variation of $(\Delta^2 - \delta^2)$ with changing distance between magnetic ions has to be calculated in the future to verify our assumption. If we know the interaction for a single pair of orbitals we can sum all the combinations presented by a three-dimensional network to get the resultant contribution. In $\text{Mn}^{2+}\text{-Cr}^{\text{III}}\text{-PBA}$ with nine AF

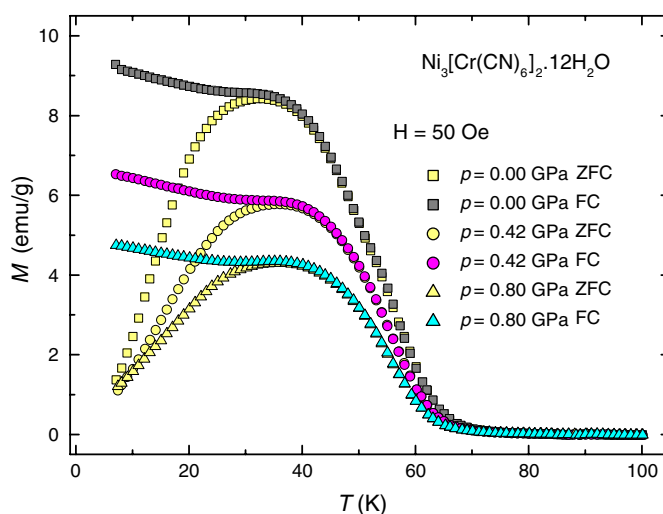


Figure 7. Magnetization $M(T)$ measured under different pressures in ZFC and FC regimes.

and six F pathways the antiferromagnetic interaction will dominate. The increase of T_C induced by higher pressure can be attributed to an increase in the super-exchange interaction J given by the increase of S and Δ in $\text{Mn}^{2+}\text{-Cr}^{\text{III}}\text{-PBA}$.

The magnetic isotherms of $\text{Ni}^{2+}\text{-Cr}^{\text{III}}\text{-PBA}$ measured under different pressures are shown in figure 6. In comparison with $\text{Mn-Cr}^{\text{III}}\text{-PBA}$ the magnetization saturates at higher magnetic field even at ambient pressure. Initial magnetization increases linearly with the applied field below $\mu_0 H = 5$ mT (see figure 7(b)), then starts to increase more steeply in an S-shape manner showing almost linear dependence above $\mu_0 H = 1$ T again. The remanent magnetization and coercive field are still small, but different from zero [4]. We suppose that the applied pressure does not change spontaneous magnetization, and only the magnetization process is significantly affected even at low temperatures ($T = 8$ K); magnetization saturates at higher magnetic fields, the region of linear increase of $M(T)$ at low fields is extended to about $\mu_0 H = 10$ mT, and the remanent magnetization M_r is slightly enhanced. The applied pressure increases the degree of tilting of octahedrons in the crystal structure, which leads to mis-orientation of magnetic moments placed on magnetic ions and to reduction of saturated magnetization.

The applied pressure reduces $M(T)$ curves measured in the ZFC and FC regimes leaving cluster-glass behaviour almost unaffected (see figure 7); the maximum T_f is slightly shifted to higher temperatures closer to bifurcation temperature T_b . Preliminary measurements indicated a small reduction of T_C under pressure $\Delta T_C/\Delta p = -3.0$ K GPa $^{-1}$, but more precise measurements revealed that the Curie temperature does not significantly change with applied pressure in the case of $\text{Ni}^{2+}\text{-Cr}^{\text{III}}\text{-PBA}$. The same results were obtained from $M(T)$ measurements performed in a lower magnetic field and from $\chi'(T)$ curves. Ni^{2+} has two unpaired d-electrons (e_g) 2 with $S = 1$ and six paired d-electrons (t_{2g}) 6 which do not contribute to magnetic interaction. Exchange coupling between the (e_g) orbital of Ni and (t_{2g}) of Cr is thus purely ferromagnetic. In the case of t_{2g} and e_g orbitals the overlap is principally zero ($\Delta = 0$) and J is not affected by pressure. No change in magnetic interaction can be expected. The applied pressure can slightly affect bonding angles between magnetic ions mediated by the cyano-bridge. A small deviation from the ideal value 180° of the bonding angle can even reduce the strength of magnetic coupling, and this results in reduction of T_C .

4. Conclusions

Our results indicate qualitatively different effects of pressure on the Curie temperature in $\text{Mn}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ with dominant antiferromagnetic super-exchange interaction and in $\text{Ni}_3^{2+}[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ with dominant ferromagnetic interaction. The applied pressure strengthens the super-exchange antiferromagnetic interaction J_{AF} . The Curie temperature T_{C} increases with the applied pressure, $\Delta T_{\text{C}}/\Delta p = 25.5 \text{ K GPa}^{-1}$, for the ferrimagnetic $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2$ system as a consequence of strengthened magnetic coupling given by increased value of the mono-electronic overlap integral S and the energy gap Δ between the mixed molecular orbitals. On the other hand the applied pressure does not significantly affect the J_{F} exchange interaction in the $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2$ ferromagnet. In real conditions the bonding angle between magnetic ions differs from the ideal value of 180° . The applied pressure can slightly affect bonding angles between magnetic ions mediated by the cyano-bridge and can reduce the strength of magnetic coupling. This phenomenon is common for both compounds, but in the case of $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2$ it is masked by the strengthened exchange interaction caused by overlapping of magnetic orbitals. The magnetization process is affected by the pressure in both compounds, but we suppose that spontaneous magnetization is not affected by pressure. Pressure-induced magnetic hardening is attributed to a change in magneto-crystalline anisotropy induced by pressure. This pressure effect is more pronounced on $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2$ where saturated magnetization μ_{s} is reduced at all temperatures, while μ_{s} is almost unaffected on $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2$ at low temperatures. The enhancement of μ_{s} in $\text{Mn}^{2+}\text{--Cr}^{\text{III}}\text{--PBA}$ in the vicinity of T_{C} is fully attributed to the strengthening of magnetic coupling.

Acknowledgments

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