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MAGNETIC MEASUREMENTS UNDER PRESSURE

Mária Zentková* – Zdeněk Arnold - Matúš Mihalik*** - Marián Mihalik* – Anton Zentko * - Jiří Kamarád** - Zuzana Mitróová* - Slavomír Maťaš***

Two different methods were used to demonstrate that high pressure is a useful tool for investigation of magnetic properties. We report on the effect of high pressure on the ferromagnetic transition in PrNi single crystal. The Curie temperature was found to increase under pressure up to 0.9 GPa with a positive pressure coefficient $\Delta T_c/\Delta p$ = 1 K/GPa. Such a behavior has been attributed to enhancement of ferromagnetic coupling between Pr ions in PrNi due to pressure induced instabilities of the crystal field singlet ground state of PrNi. The measurement was realized by transformer method. Additionally, the effect of pressure on magnetic properties of $Cr_3[Cr(CN)_6]_2$ x 15 H_2O has been studied by means of SQUID magnetometry. Observed increase of Curie temperature with the pressure coefficient $\Delta T_c/\Delta p$ = 26 K/GPa can be explained by pressure induced increased overlapping of magnetic orbitals.

Keywords: hydrostatic pressure, Prussian blue analogues, intermetallic compound, ferromagnetism, ferrimagnetism.

1 INTRODUCTION

Usual motivation for applying the pressure during magnetic measurements is mostly based on the fact that the pressure affects microscopic quantities like electronic density of states, bandwidths, resulting in change of magnetic moments together with wide scale changing of critical temperatures including the Curie temperature T_C. In our paper we demonstrate magnetic measurements under pressure on two kinds of samples – metallic sample of PrNi single crystal and a set of dielectric samples prepared on the base of Prussian blue analogues (PBA) .

2 THE EFFECT OF PRESSURE ON PrNi SINGLE CRYSTAL

In intermetallic compound PrNi magnetic ordering occurs not through the usual process of alignment of moments, but rather through polarization instability of the crystal field (CF) singlet ground state. The compound crystallizes in the orthorhombic CrB-type structure (space group *Cmcm*).

Fig. 1. Piston cylinder type of CuBe pressure cell used in transformer method measurements. From right: lead-through with wires and manganin; cylinder – filled with mineral oil; piston maintains pressure in the cell.

Unit cell dimensions: a = 0.38307(9), b = 1.0543(2), c = 0.4369(1) nm and unit cell volume 0.17644(7) nm^3 [1]. The local symmetry of the Pr site (point group C_{2v}) completely removes the degeneracy of the ground 4f multiplet (J = 4). The CF interaction splits this multiplet into nine singlets. In spite of the singlet ground state in PrNi, due to the low symmetry at the Pr site, PrNi undergoes ferromagnetic transition at T_C = 20.5 K [2]. The CF transitions in PrNi have a cooperative character and propagate through the crystal due to the exchange coupling between the Pr ions. Ni is nonmagnetic in this compound.

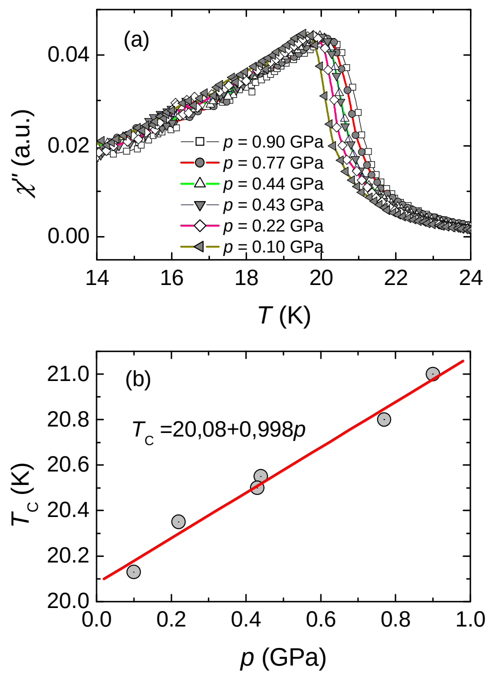

Fig. 2. The effect of pressure on out of the phase AC susceptibility (a). The Curie temperature increases with pressure (b).

The effect of pressure on ferromagnetic transition in PrNi single crystal has been studied by transformer method [3]. The temperature in the range from 3.5 K to 300 K was varied by two-stage close-cycle helium refrigerator. In this device the room temperature helium gas is first compressed, and then supplied to the refrigerator via flexible gas lines. The compressed helium is cooled by expansion, and provides cooling to heat station on the refrigerator. After cooling the refrigerator, the gas is re-

*Institute of Experimental Physics Slovak Academy of Sciences , Watsonova 47, 040 00 Košice, Slovakia , E-mail: zentkova@saske.sk
**Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, CZ-162 53 Praha 6,Czech Republic
***Charles University, Faculty of Mathematics and Physics, Department of Electronic Structures, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

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turned to the compressor to repeat the cycle. The temperature was measured by two diodes used as thermometers placed outside the pressure chamber. Hydraulic pressure up to 0.9 GPa was generated by a standard Cu–Be piston cylinder device filled with the mixture of mineral oils as a pressure transmitting medium (Fig. 1). The pressure inside the chamber was measured using a manganin pressure sensor based on the well known change of the manganin resistance under pressure. The effect of pressure was studied by means of AC susceptibility measurements. The transition to ferromagnetic state is indicated by an increase in $\chi'(T)$ and $\chi''(T)$ curves below $T = 24$ K. The Curie temperature T_C was determined as an inflection point (a minimum on $d\chi'/dT$ and $d\chi''/dT$ curves). The typical $\chi''(T)$ curves in vicinity of T_C are shown in Fig.2(a). As can be seen from Fig. 2.(b) the applied pres-sure shifts T_C nearly linearly to higher temperatures with pressure coefficient $dT_C/dp = 1$ K/GPa. The pressure induced increase of T_c indicates enhancement of ferromagnetic coupling between Pr ions in PrNi, which can be attributed to pressure induced instabilities of the crystal field singlet ground state of PrNi.

3 THE EFFECT OF PRESSURE ON MAGNETIC PROPERTIES OF $Cr^{2+}_3[Cr^{III}(CN)_6]_2.nH_2O$

Investigated $Cr^{2+}_3[Cr^{III}(CN)_6]_2.nH_2O$ belongs to the so called Prussian blue analogues, that means the family of compounds with general formula $A_x[B(CN)_6]_y.nH_2O$, where A and B are ions of 3d metals. Prussian blue analogues have been subject of interest mostly because of high sensitivity of their magnetic properties on different types of external stimuli.

Magnetic properties of Prussian blue analogues can be analyzed within two simplifications: (a): Only the superexchange interactions between the nearest neighbour metal ions have to be considered. (b): The character of superexchange interactions can be easily predicted from a simple orbital symmetry rule. When the magnetic orbital symmetries of the metal ions are the same, the superexchange interaction is antiferromagnetic (J_{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 Prussian blue analogue $TM^{2+}_3[Cr^{III}(CN)_6]_2.nH_2O$ system, TM^{2+} is 3d ion [4]. Magnetization measurements performed on Prussian blue analogues $TM^{2+}_3[Cr^{III}(CN)_6]_2.nH_2O$ (TM = Cr, Mn, Fe, Co, Ni, Cu) confirmed the dual character of exchange interaction (J_{AF} and J_F) in this system. J_{AF} interaction dominates for Cr^{2+} sample resulting in ferrimagnetic ordering and with rising atomic number Z the J_F interaction becomes more important reaching pure ferromagnetic character for Cu^{2+} sample [5]. Investigated compound $Cr^{2+}_3[C^{rIII}(CN)_6]_2.nH_2O$ adopts cubic crystal structure, space group is Fm-3m (No 225) with lattice parameter a = 1.03805(9) nm. As the unit cell should correspond to 1 and 1/3 formula unit, 1/3 of $Cr(CN)_6$ positions are statistically vacant or filled with water. Cr^{III} in anion $[Cr^{III}(CN)_6]^{3-}$ is low spin and has only $(t_{2g})^3$ orbitals and the spin S = 3/2. On the other hand we can suppose for cation Cr^{2+} two possibilities, more probable state where 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. In the case of pure antiferromagnetic superexchange interaction and supposing all Cr^{2+} are high spin, the expected theoretical value of spontaneous magnetization $\mu_s = g[3S(Cr^{2+}) - 2S(Cr^{III})] = 6\ \mu_B$; g = 2 is the Lande factor. The experimentally determined value $\mu_s(\exp) = 1.73\ \mu_B$ [5] is much smaller than theoretical one indicating that a part of Cr^{2+} are low spin (S = 1) yielding total compensation of spins $\mu_s = 0\ \mu_B$.

Fig. 3. Piston cylinder type of CuBe pressure cell used in SQUID magnetometer.

Pressure was generated by a standard CuBe pressure cell operating up to 1.2 GPa (see Fig.3). Actual pressure was determined from the pressure dependence $T_c(p)$ of the superconducting transition of the high purity lead (see Fig.4; $T_c = 7.135$ K at ambient pressure). The decrease of the pressure in the cell with decreasing temperature is due to the higher thermal expansion of cell than that of mineral oil. Correction on actual pressure at about 60 K was made (see Fig.5). In the case of SQUID measurements the pressure cell itself contributes to overall magnetization by a diamagnetic contribution which can not be subtracted directly. Experimental data presented in the paper are not corrected on diamagnetic signal of the pressure cell. The powder sample with mass of about 5 mg was placed into cylindrical holder 5 mm long and with the diameter of 3 mm. The pressure was always applied at the room temperature. The experiment started with the highest pressure, which was then gradually decreased by 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. 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).

Fig.6. shows magnetization curves of Cr^{2+}-Cr^{III}-PBA measured at T = 6 K. Magnetization has tendency to saturate in very low magnetic fields increasing at first very steep then has large curvature and above $\mu_0 H = 1$ T is almost linearly dependent on rising magnetic field. The remanent magnetization μ_r and coercive force H_c for this material are close to zero [5].

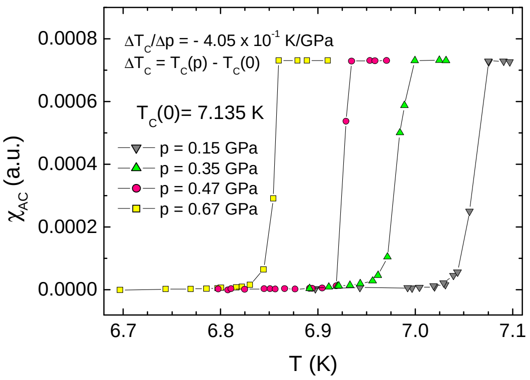

Fig. 4. Pressure dependence of superconducting transition of high purity Pb.

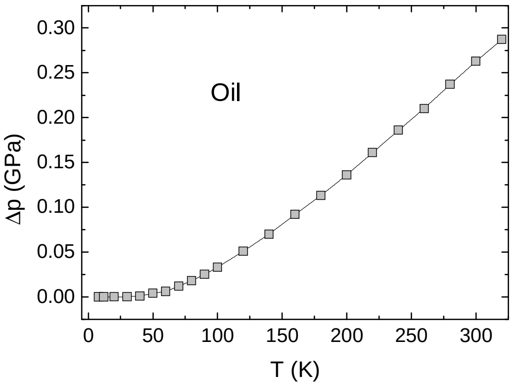

Fig. 5. Reduction of pressure inside the pressure cell by cooling to lower temperatures (b).

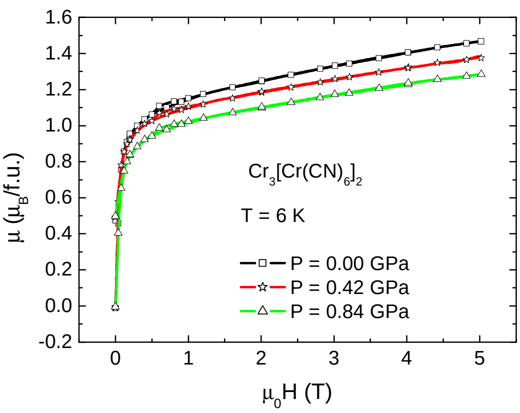

Fig.6. Pressure induces a decrease of magnetization.

The applied pressure induces the decrease of the saturated magnetization. Effect of pressure on magnetization can be attributed to structural changes and to pressure induced population of Cr^{2+} in low spin states. Both ions Cr^{2+} and Cr^{III} are in octahedral position in the crystal structure and super-exchange pathway is mediated via cyano-bridge Cr^{2+} – N≡C – Cr^{III}. It is expected that magnetic moments are oriented along the main axes of octahedrons by anti-parallel way and the most effective super-exchange interaction is if the angle of the pathway is 180 degrees. There is an indication coming from structural analysis that the angle of the pathway is less than 180 degrees and that axes of polyhedrons are tilted in real case. The applied pressure generates deformation of the polyhedrons resulting in a change of CF effect and makes tilting of these polyhedrons more pronounced leading to reduction of saturated magnetic moment and the strength of super-exchange interaction.

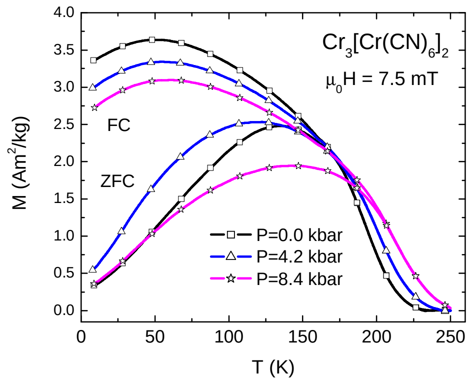

Fig.7. Pressure induces changes in temperature dependence of magnetization M (T).

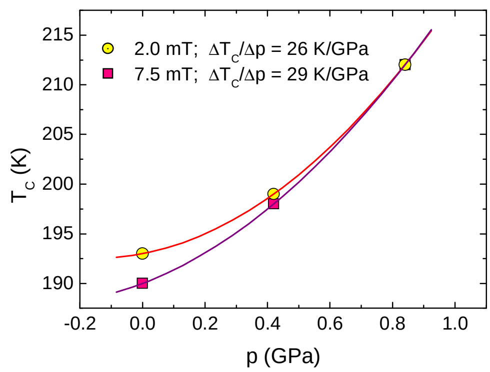

Fig.8. Pressure induces an increase of the Curie temperature determined from M(T) measured at magnetic field with two different magnetic induction.

The transition to magnetically ordered state is accompanied by a steep increase of M(T) (see Fig.7). The Curie temperature T_C we define as an inflection point of M(T) curve in this region. The applied pressure shifts T_C to higher temperatures in almost parabolic way in this region of applied pressures. The estimated positive coefficient $\Delta T_C/\Delta p$ = 26 K/GPa or $\Delta T_C/\Delta p$ = 29 K/GPa (see Fig.8) are the highest changes of T_C with pressure which was up to now published on any PBA. The positive pressure coefficients $\Delta T_C/\Delta p \approx$ 14 K/GPa and $\Delta T_C/\Delta p \approx$ 11 K/GPa were recently reported for $[Mn(en)]_3[Cr(CN)_6]_2{\cdot}4H_2O$ [6] and for $Mn_3^{2+}[Mn^{III}(CN)_6]_2{\cdot}12H_2O{\cdot}1.7(CH_3OH)$ [7] Mn-based PBA ferrimagnets. Characteristic feature of many PBA – a hysteretic behavior between zero field cooled (ZFC) and z field cooled (FC) magnetization in low magnetic fields was observed on Cr^{2+}-Cr^{III}-PBA (see Fig.7). Difference between M(T) measured in ZFC and FC regime indicates region of irreversible behavior of magnetization processes. 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 field cooled FC measurements. The reduced value of magnetization $M(T)$ in ZFC regime can indicate a change in CF effect leading to a change of magnetocrystalline anisotropy.

From the extended Hückel calculations performed in [8] follows that the antiferromagnetic contribution to the coupling J is given approximately by the expression 2 S $(\Delta^2 - \delta^2)^{1/2}$, where δ is the energy gap between the (unmixed) ***a*** and ***b*** orbitals, Δ is the energy gap between the molecular orbitals built from them, and S is the monoelectronic overlap integral between ***a*** and ***b***. The antiferromagnetic term can 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 length of exchange path $Cr^{2+} - N{\equiv}C - Cr^{III}$ and increases overlap integral S. The applied pressure can increase Δ leading to an increase of both terms $(\Delta - \delta)$, $(\Delta + \delta)$ and this way leads to strengthening of the antiferromagnetic coupling. The term $(\Delta^2 - \delta^2)$ was calculated for number of TM^{2+} and TM^{III} with assumption that the distance between magnetic ions is the same [8]; variation of $(\Delta^2 - \delta^2)$ with changing distance between magnetic ions has to be calculated in the future to verify this conclusion.

4 CONCLUSIONS

Our study clearly demonstrates that CuBe pressure cell is powerful tool to study pressure effect on the Curie temperature in helium close cycle system by - initial permeability measurements using a transformer method or magnetization, DC and AC susceptibility in commercial SQUID magnetometer. The Curie temperature increases under pressure with a positive pressure coefficient $\Delta T_c/\Delta p$ = 1 K/GPa in the case of PrNi single crystal. Such a behavior is attributed to enhancement of ferromagnetic coupling between Pr ions in PrNi due to pressure induced instabilities of the crystal field singlet ground state of PrNi. Magnetization process is affected by pressure in the case of $Cr_3[Cr(CN)_6]_2$ compound. The reduction of saturated magnetization can be attributed to pressure generated population of Cr^{2+} low spin ions and to pressure induced tilting of polyhedrons in the crystal structure. The applied pressure strengthens super-exchange antiferromagnetic interaction J_{AF}, the Curie temperature T_C increases with the applied pressure, $\Delta T_C/\Delta p$ = 29 K/GPa as a consequence of strengthened magnetic coupling given by increased value of the monoelectronic overlap integral S and energy gap Δ between the mixed molecular orbitals.

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Mária Zentková (Dr.**)**, graduated from Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic, interested in the study of molecule-based magnetic materials.

Zdeněk Arnold (Dr.**),** graduated from Charles University, Prague, Czech Republic, involved in the experimental study of pressure effects on magnetic phase transitions.

Matúš Mihalik (Ing.**)**, PhD student at Faculty of Mathematics and Physics, Charles University, Prague. Interested in magnetic properties of strongly correlated electron systems.

Marián Mihalik (Dr.**)**, graduated from Faculty of Sciences in Košice. His interests are heavy fermion systems and molecular magnets.

Anton Zentko, (Dr.**,** DrSc.**)**, graduated from Czech Technical University, Prague, envolved in study of materials under high magnetic fields and pressures.

Jiří Kamarád (Dr.**),** graduated from the Czech Technical University, Prague. He is involved in scientific projects devoted to physics of solids under high pressure, high pressure techniques.

Zuzana Mitróová (Dr.**)**, graduated from the Faculty of Chemical Engineering, Technical University, Bratislava, involved in solid state chemistry and of the Prussian blue analogues.

Slavomír Maťaš (Dr.**)**, graduated from the Faculty of Sciences in Košice. He has been involved to scientific projects devoted to study strong-electron correlation in various systems.