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Mediation of Magnetic Interactions in Prussian Blue Family*

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Results of the AC susceptibility and DC magnetization of the family $ACo[Fe(CN)_6]$ for different cations A: Li, Na, K, Rb, Cs, NH_4, $N(Et)_4$ are presented. Differences in magnetic properties are found that can be attributed to an indirect interaction mediated by the cations. Two other compounds: $A_2Ni^{II}[Fe^{II}(CN)_6]$ (A = K, Na) were also studied. The strong influence on magnetic properties due to alkaline cations was again observed.

Key words: molecular magnets, Prussian blue, hexacyanometalates, magnetic susceptibility

In the last decade a great progress has been observed in the field of new magnetic materials built from molecular blocks [1]. Among these new materials a very important role is reserved for the 3d hexacyano coordination compounds, called also Prussian blue family [2,3]. The original Prussian blue $KFe^{III}[Fe^{II}(CN)_6]$ was probably the first molecular compound ever reported [4].

The general formula for this family is $AM''[M'(CN_6)]xH_2O$, where M′ and M″ denote 3d ions, A is an additional, non magnetic ion, which assures null net charge of the unit cell. The crystal structure is very simple as shown in Figure 1.

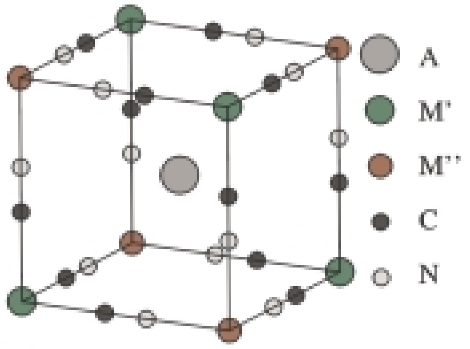

Figure 1. Crystal structure of Prussian blue. Figure shows 1/8 of the unit cell [5].

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*Dedicated to the memory of Professor Krzysztof Pigoń.

The M′–CN–M″ bridges form 3 dimensional crystal network with the perfect order of CN$^-$ ions. M′ are always coordinated by C and are in low spin state, while M″ ions are in high spin state. The tetrahedral site inside the cube is occupied by ions A or by water molecules. Usually there is some disorder in the tetrahedral sites: not all of them are occupied. Magnetic properties of the Prussian blue family seem to be well understood [2,5]. Magnetic orbitals of both M′ and M″ are of nonbonding, sometimes antibonding character. If they are orthogonal only ferromagnetic coupling is present, in the case of non orthogonal magnetic orbitals antiferromagnetic coupling takes place, which is usually much stronger. Magnetic ordering appears also in the compounds with non 3d M'' metal center. Recently, the study on the magnetic properties of the uranium hexacyanomanganate [6] revealed the ferrimagnetic transition at T_c = 36.8 K. Attractive perspectives for the Prussian blue analogues, connected with photoinduced magnetism, were recently discovered. Hashimoto *et al.* [7] revealed that the T_c in Co^{II}Fe^{III} complex increases after irradiation with red light beam. The possible explanation is that isolated diamagnetic Co^{III}Fe^{II} pairs are transformed by light induced charge transfer to the Co^{II}Fe^{III} state, in which both 3d metals posses magnetic moment. Exchange mechanism mentioned above let different authors to synthesize new high temperature molecular magnets based on cyano bridges [8,9]. There are, however, other factors influencing the magnetic properties of the hexacyanometalates. The problem, which is still not completely understood, is connected with disorder. Substances from this family show a behavior similar to spin glasses [10] and those with highest Curie point are often non stoichiometric. All of the above mentioned studies were devoted to the M′–M″ magnetic interactions mediated by the CN$^-$ bridges. Relatively little attention was paid to the non magnetic cations in the tetrahedral positions.

Our previous paper [10] was dealing with magnetic properties of $KCo^{II}[Fe^{III}(CN)_6]$, which shows long range magnetic ordering below 13.7 K. In the present paper we report results of AC susceptibility and DC magnetization for the following cations: Li, Na, K, Rb, Cs, NH_4 and $N(Et)_4$, where Et denotes C_2H_5. In addition, magnetic data for two complexes with non magnetic M′ center $A_2Ni^{II}[Fe^{II}(CN)_6]$ are included.

EXPERIMENTAL

$KCo[Fe(CN)_6]$ was prepared by adding 100 cm^3 of 0.1M $Co(NO_3)_2$ aqueous solution to 50 cm^3 of 0.1 M $K_3[Fe(CN)_6]$ solution. An amorphous precipitate of $KCo[Fe(CN)_6]$ was paper-filtered and washed several times with distilled water. The precipitate was dried in 25°C, granulated, washed again and dried. Complex compounds of the formula: $LiCo[Fe(CN)_6]$, $NaCo[Fe(CN)_6]$, $RbCo[Fe(CN)_6]$, $CsCo[Fe(CN)_6]$, $(NH)_4Co[Fe(CN)_6]$ and $N(Et)_4Co[Fe(CN)_6]$ were obtained from $KCo[Fe(CN)_6]$ by exchange of K^+ ions on Li^+, Na^+, Rb^+, Cs^+, $(NH)_4^+$ and $N(Et)_4^+$ respectively, from their concentrated solutions. The samples in the form of dark, very fine powder and mass *ca.* 0.1 g were used. As the synthesis procedure was the same for all our samples we assumed that the water content is about the same in all of them.

All measurements were performed on Lake Shore 7225 instrument enabling both AC and DC operating modes. In the AC mode complex susceptibility as a function of frequency in the range 5–1000 Hz was measured in the wide range of temperatures. The measurement of susceptibility as a function of the amplitude of the applied AC field gives information about non linear response of the sample. In the DC mode the magnetization as a function of the applied static field in the range up to 5 Tesla was measured.

RESULTS AND DISCUSSION

Complexes of the family $ACo^{II}[Fe^{III}(CN)_6]$: Results of measurements of the complex AC susceptibility $\chi = \chi' - i\chi''$ in the neighborhood of the phase transition are shown in Figure 2. The curve presented in [10] for $KCo[Fe(CN)_6]$ is also included. One can observe relatively large changes in the character of the anomaly connected with magnetic ordering. Both the position of the anomaly and its magnitude change for samples with different cations. In addition, changes in real part of χ are not reflected in imaginary component. Magnetic transition point, determined as the temperature of χ' maximum (for f = 5 Hz) varies from T_c = 12.9 K for Cs to T_c = 14.6 K for the Na compound. Table 1 gives T_c values for all cations used.

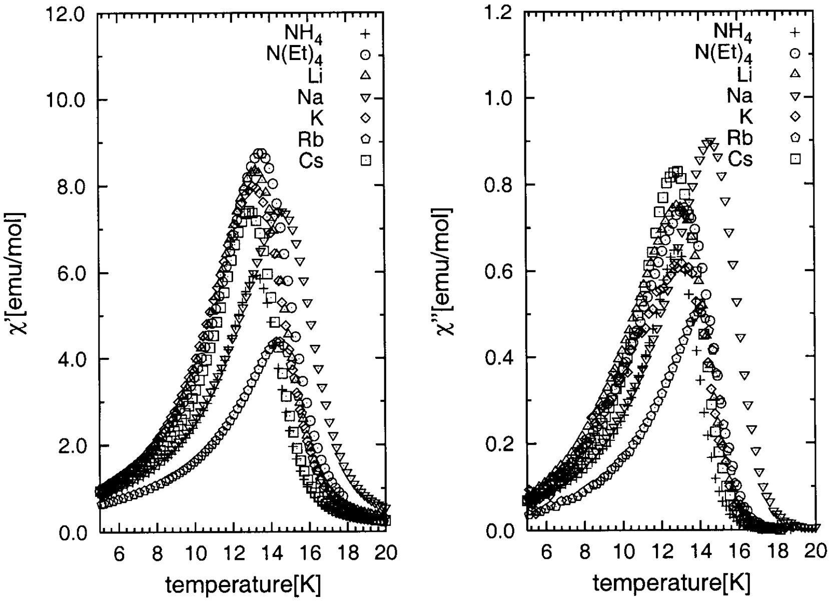

Figure 2. Real (left) and imaginary (right) parts of complex magnetic susceptibility of $ACo^{II}[Fe^{III}(CN)_6]$ family with different cations A measured at frequency f = 5 Hz.

Table 1. Magnetic properties of some compounds in $ACo^{II}[Fe^{III}(CN)_6]$ family.

ion A	ionic radius [Å]	T_c [K]	H_c [Oe]	M_R [μ_B]
Li^+	0.68	13.2	0.756	0.1035
Na^+	0.97	14.6	1.1887	0.1361
K^+	1.33	13.7	0.9267	0.1420
Rb^+	1.47	14.5	1.03	0.0694
Cs^+	1.67	12.9	0.863	0.0947
NH_4^+	1.61	13.3	0.869	0.0778
$N(Et)_4^+$		13.6	0.935	0.1292

The frequency dependence of complex susceptibility for $KCo^{II}[Fe^{III}(CN)_6]$ [11] pointed to the glassy behavior. Our present study leads to the same conclusion. The frequency dependence of the susceptibility for rubidium sample, shown in Figure 3, exemplifies a typical behavior for the whole family. The χ'' contribution amounts up to 10% of χ', which is understandable for a system with structural disorder and complex relaxation phenomena.

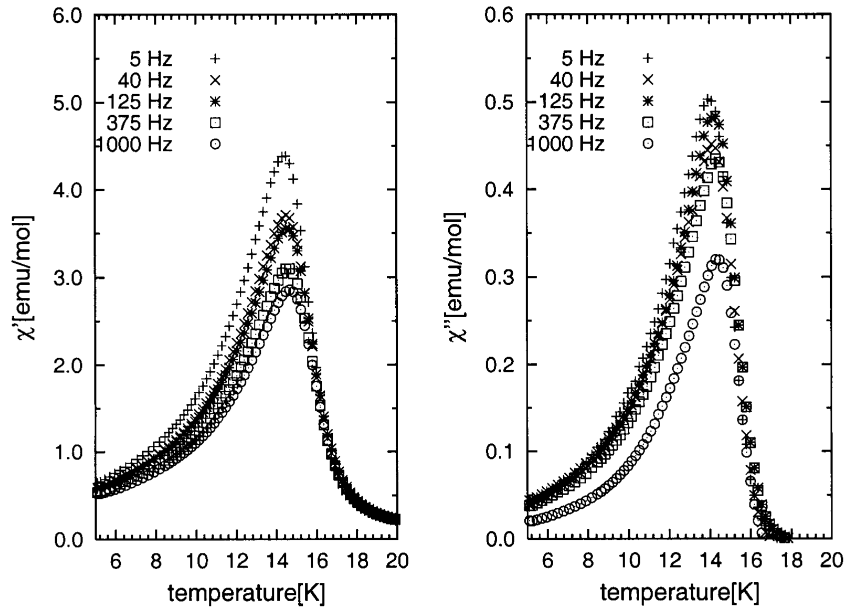

Figure 3. Real (left) and imaginary (right) parts of complex magnetic susceptibility of $RbCo^{II}[Fe^{III}(CN)_6]$ for different frequencies as the function of temperature.

It is also interesting that the non magnetic ion influences the hysteresis loops and magnetization curves. Figure 4 compels hysteresis loops measured at 4.2 K. Small but well defined differences again are observed. In Table 1 we present coercivity H_c and magnetic remanence M_R for all the samples under study. The data clearly indicate that magnetic properties do not change monotonically with ionic radius.

Figure 5 presents magnetization curves up to 56 kOe in the same temperature. All the curves show that the samples are not saturated yet. The expected saturation spin only value is 2 μ_B/mol. The excess magnetization may come from possible orbital contribution.

Complexes of the family $A_2Ni^{II}[Fe^{II}(CN)_6]$: The situation is even more interesting in the case of low spin Fe^{II}, which is diamagnetic (s = 0). Now, the only magnetic response comes in principle from Ni (s = 1). Like in the original Prussian blue, the magnetic interactions occur between next-nearest ions through the M″–NC–M′–CN–M″ linkages. The possible path of magnetic interaction is also *via* alkali cation: Ni–A–Ni.

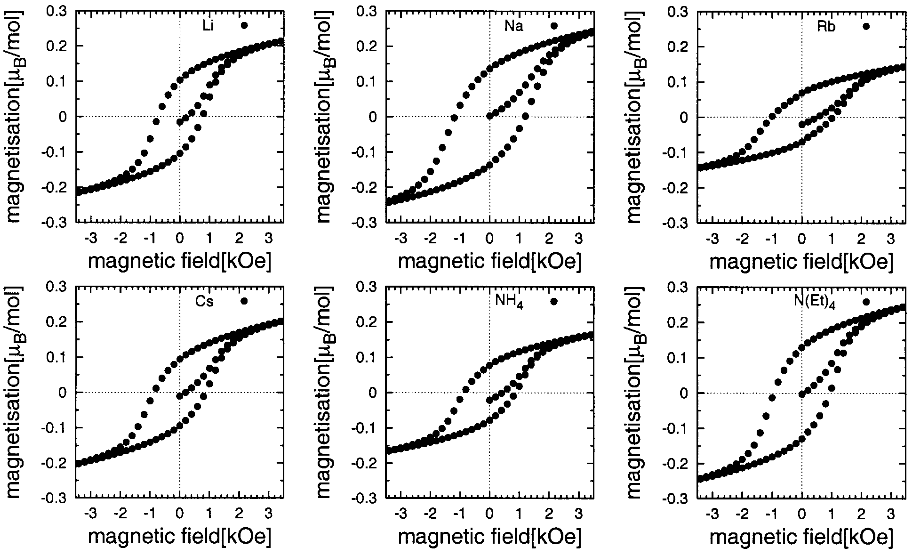

Figure 4. Histeresis loops for compounds with different cations at 4.2 K.

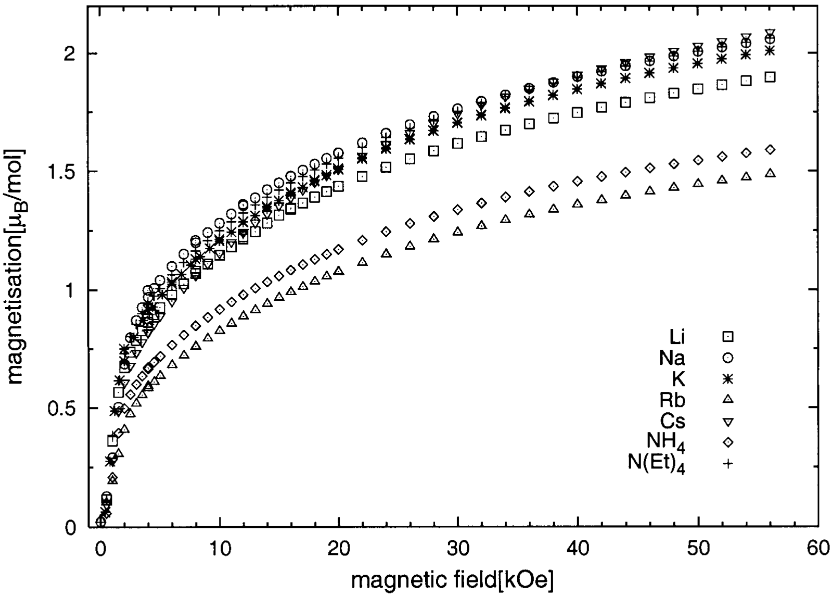

Figure 5. Magnetization curves for compounds with different cations at 4.2 K.

Moreover, there are twice as many cations as before so all tetrahedral sites are occupied. We present results for two different cations: sodium and potassium. The difference between the two compounds is astonishing.

Figure 6 shows temperature dependence of $\chi'\cdot T$ and χ'' for A = K and Na. In both cases $\chi'\cdot T$ increases with decreasing temperature what indicates remarkable correlations of magnetic moments. Compound with Na cations shows much greater $\chi'\cdot T$ increase than the one with K cation. In addition, there is a bump in χT dependence on temperature at about 10 K. This behavior is reflected in sharp peak in imaginary susceptibility χ''. We performed the study of the susceptibility dependence on the amplitude of AC field (see Figure 7). One can observe that the real part of susceptibility depends on the amplitude of H_{AC} below the anomaly at 10 K, while no such a dependence is seen for χ''. This fact indicates that the response of the sample below 10 K is highly non linear.

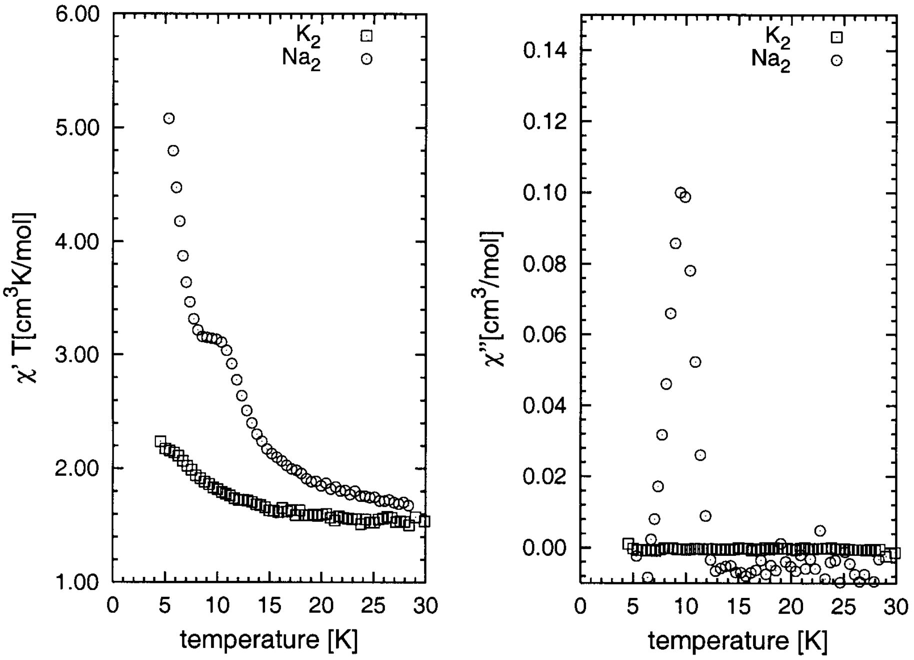

Figure 6. Real (left) and imaginary (right) parts of complex magnetic susceptibility of $A_2Ni^{II}[Fe^{II}(CN)_6]$ family with different cations measured at frequency f = 5 Hz.

The results presented above show that the non magnetic cation plays a role in magnetic properties. The low spin Fe^{III} (s = 1/2) is in state ${}^2T_{2g}$ (magnetic orbital t_{2g}), while Co^{II} is in high spin state (s = 3/2) ${}^4T_{1g}$ (magnetic orbital t_{2g}, e_g). According to what was mentioned in the introduction, there is antiferromagnetic coupling between nearest Fe and Co *via* CN link. The distance Fe–CN–Co is ≈ 5 Å. Assuming a perfect octahedral crystal field on 3d ion, one gets six equivalent couplings. There are also

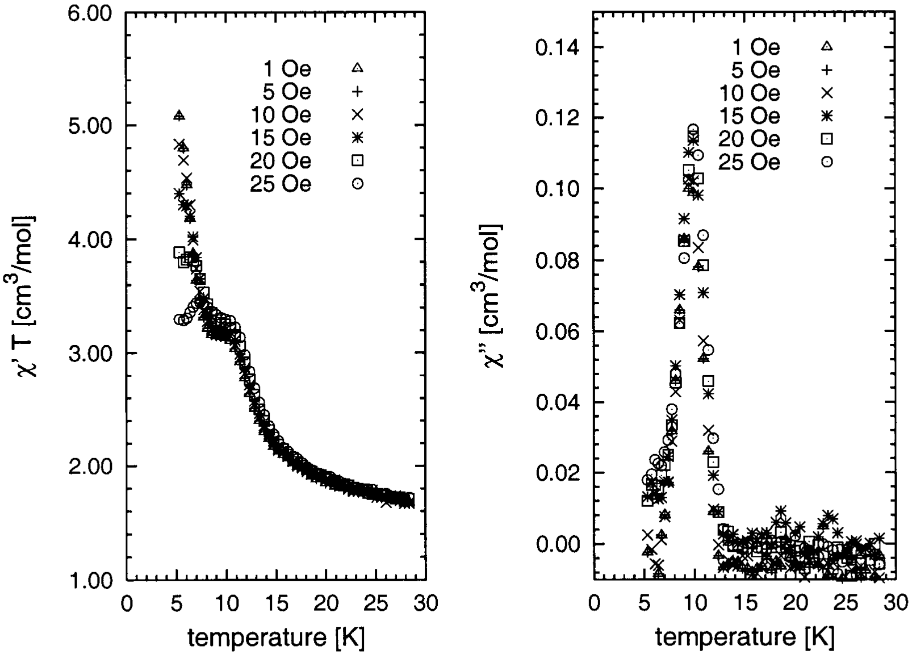

Figure 7. Complex susceptibility of $Na_2Ni[Fe(CN)_6]$ measured for frequency f = 5 Hz and different driving fields H_{AC}.

eight possible tetrahedral sites, half of them occupied by non magnetic cations. Every cation gives path to possible couplings with remaining seven 3d ions. The indirect interaction is over the distance $\approx 5\sqrt{3}$ Å and at an angle 109.5°. One cannot exclude that this type of interaction, which is of course much weaker, makes slight modification of the interaction mediated by CN. When one of the 3d centers is silent (low spin Fe^{II}, s = 0) this additional interaction becomes more visible. The anomaly of χ'' for $Na_2Ni^{II}[Fe^{II}(CN)_6]$ takes place at T = 10 K.

CONCLUSIONS

AC susceptibility and DC magnetization was measured for series of ferrimagnetic $ACo^{II}[Fe^{III}(CN)_6]\times H_2O$ compounds with A = Li, Na, K, Rb, Cs, NH_4 and $N(Et)_4$. The study was aimed at investigating the role of nonmagnetic cations in mediation of magnetic interactions between 3d metals. The differences in ordering temperatures, coercivity and remanence were found; however, there was no systematic tendency nor dependence on ionic radius observed. Additionally, two compounds $Na_2Ni^{II}[Fe^{II}(CN)_6]$ and $K_2Ni^{II}[Fe^{II}(CN)_6]$, where only Ni ion has a magnetic moment, were studied. While the potassium sample was an ordinary paramagnetic, the Na sample showed an interesting behavior with the bump on $\chi'\cdot T$ curve and a χ'' peak.

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