MOLECULE-BASED MAGNETIC MATERIALS

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SUMMARY

In the article we intend to present some recent achievements in the chemistry and physics of 3d and f electron mixed valence systems based on the Prussian blue in the field of molecular magnetism. Prussian blue is sometimes considered as the first coordination compound and in the paper we would like to demonstrate how it is possible to obtain completely new results based on the old one compound.

Keywords: *Molecular magnets, Prussian Blue analogues, magnetic interactions, photomagnetism .*

1. INTRODUCTION

The story of Prussian blue, which is sometimes considered as the first coordination compound, has begun in 1704 when a Berliner draper M. Diesbach prepared for the first time a bright blue pigment when he simply boiled beef blood in a strongly basic medium and was surprised to get a blue coloration [1]. Nowadays, the Prussian blue is usually prepared from aqueous solutions of hexacyanoferrate(II) and iron(III) chloride. A lecture demonstration consists in placing on one side of a Petri dish a few crystals of potassium hexacyanoferrate(II) and at the opposite a few crystals of iron(III) chloride. Water is then poured in between so that the crystals are slowly dipped in water. A beautiful blue color develops, after a while, at the interface where convexion movement brings together the dissolved reactants. Such a simple experiment can be used for demonstration of the fact that Prussian blue and its derivatives can be used as industrial pigments as well as that a mild chemistry at room temperature and pressure can be used in aqueous solutions to build solids from molecules [2].

The chemical formula of Prussian blue is $Fe(III)_4[Fe(II)(CN)_6]_3.14\ H_2O$ [3]. Its structure was first proposed by Keggin and Miles [4] and later modified by Ludi and Güdel in [5]. Ideal structure of Prussian blue is displayed on the Figure 1. The real structure is much more complicated especially because of the water molecules present at two different positions in the lattice. From 14 water molecules present in the lattice 6 are coordinated to Fe(III) ion, distance Fe(III) – O is 1.95 Å and 8 water molecules are placed isolated in the centre of elementary cell octants or bridged by means of hydrogen bonds to coordination water (Fig.2.). The lattice is not free from the vacancies arising due to the non-stoichiometric ratio between the low spin Fe(II) and high spin Fe(III) ions. This kind of a disorder is typical for majority of the members of Prussian blue analogues family.
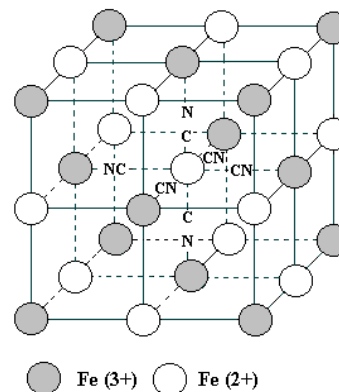
Fig. 1 Typical hexacyanoferrate complex in which ferrous and ferric ion are coordinated through cyanide ligands. The lines between irons represent the cyanide ligands [13].
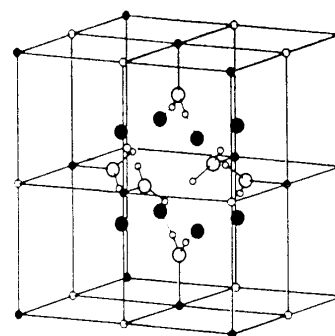
Fig. 2 The unit cell of Prussian blue displaying part of the hydrogen-bond network. Cyanide ions are omitted for the sake of clarity and the radii of the atoms are chosen arbitrarily (● Fe(II), ○ Fe(III), ○ O and ○ H of coordination water, ● O) [7].

A Prussian blue analogues are compounds with chemical formula $C_nA_x[B(CN)_6]_y.zH_2O$ where A occupies all the summits and all the centres of the faces and the $[B(CN)_6]^-$ are located at the octahedral sites. C is monovalent cation, which can be inserted in part of the tetrahedral sites of the cubic structure. The following structure modifications may appear: A/B 1:1 stoichiometry, when the coordination spheres of A and B are $A(NC)_6$ and $B(CN)_6$ A(B) has six B(A) neighbors, and A/B 3:2 stoichiometry with one third of $B(CN)_6$ vacancies filled by water molecules. The B coordination sphere is left unchanged but the mean coordination sphere of A becomes $A(NC)_4(H_2O)_2$, so the mean number of B neighbors around A is now four. The 3d based Prussian blue analogues usually present a cell parameter ranging from 10.0 to 10.9 Å [5]. This value corresponds to the A − A (B − B) distances between two identical metallic ions in the network. In the Prussian blue itself the Fe(III) cations are divided by 10.18 Å separated by the $[Fe(II)(CN_6)]^{4-}$ entities [3], therefore the material behaves as paramagnet with weak interactions between two neighboring magnetic centers, which are high spin d^5 Fe(III) (S=5/2) ; Fe(II) d^6 centers are low spin and diamagnetic. Nevertheless, the −{NC-Fe(II)-CN}- bridge between two Fe(III) ions provides some electron delocalization pathway studied by Day and Robin [6] and below 5.6 K is Prussian blue ferromagnetically ordered [7]. The magnetic coupling of metals in Prussian blue analogues is described in terms of a superexchange mechanism through the cyanide ligands. The superexchange mechanism is summarized on the basis of the Goodenough-Kanamori rule [8-10], which includes consideration of the bond angle and the symmetry of the metal and ligand orbitals concerned. There are two mechanisms for superexchange interactions: the kinetic exchange mechanism (J_{KE}) and the potential exchange mechanism (J_{PE}) [11]. The kinetic exchange is mediated by a direct pathway of the overlapping orbitals, which connects the two interacting magnetic orbitals. It is antiferromagnetic as a consequence of the Pauli principle, leading to antiparallel spin ordering via covalent bond. Potential exchange is effective between orthogonal magnetic orbitals with comparable orbital energy. In this case Hund's rule leads to a parallel spin alignment, which means a ferromagnetic interaction. In the case of Prussian blue analogues the metal d orbitals are split into the t $_{2g}$ and e_g sets by the CN ligands. Therefore based on the magnetic orbital symmetry we can predict whether the orbital superexchange among each of the orbitals on metal ions is J_{KE} or J_{PE}. When the magnetic orbital symmetries of the metals are the same, the superexchange interaction is J_{KE}. When the magnetic orbital symmetries of the metals are different, the superexchange interaction is J_{PE}. The total superexchange interaction is given by the sum of all

of orbital exchange contributions between the transition metal ions [12].

2. ANALOGUES CONTAINING 3d- OR 4f − AND 5f- ELECTRON ION

2.1. $C_nA_x[Fe(CN)_6]$ family

The frequently discussed representant of the family of Prussian blue analogues is $KCo[Fe(CN)_6].6H_2O$. It crystallizes in a face centered cubic structure with lattice parameter a = 9.96 Å. The real structure of cobalt hexafericyanide is in reality much more complicated including interstitial ions of potassium, vacancies filled with water molecules and interstitial water molecules. Cobalt ions are present in two oxidation states as Co(III) and Co(II). Coordination of one cobalt ion is $Co(N_6)$ and three other Co ions are coordinated $Co(N_4O_2)$ [14]. The effective magnetic moment μ_{eff} was calculated from Curie constant and is equal 5.7 μ_B [15]. The value of effective magnetic moment estimated from spins of Co and Fe ions is 4.25 μ_B . The value of coercive field H_c is 930 Oe at temperature 4.2 K, and saturated magnetization $M_s = 2500$ cm^3G/mol [15, 16]. Obtained values are however strongly dependent on the synthesis conditions, which influences number of vacancies in the lattice as well as how many vacancies are filled with water. The presence of coordination water decreases the values of magnetic saturation. The transition from magnetically ordered state occurs at temperature varying from 14 K to 17 K [15, 16, and other]. A surprising effect was observed by Sato *et al.* [17]. It was observed and later confirmed by many other groups [18, 19] that illumination of the sample by red light beam leads to increase of magnetic transition temperature T_C as well as the values of saturated magnetization, coercive field and remanent magnetization. The process was found to be reversible, after consequent illumination with blue light the initial state was reestablished. Sato has ascribed observed process to the photoinduced change in oxidation states of Fe and Co. Magnetic ordering in compound is established by means of photoinduced electron transfer through the molecular bridge Co − C ≡ N - Fe. Ions of Co(III) and Fe (II) were both low spin and diamagnetic before illumination. After illumination they change to high spin Fe(III) and Co(II) and therefore the total number of magnetic neighbors in the lattice is increased. This effect is a promising for the future applications of this kind of materials as e.g. photomagnetic switches, however the magnetic transition temperature T_C at which the effect is observed is very low and the response of the system after illumunation slow. It is clear that the presence of potassium ion in the lattice is playing an

important role in photoinduced magnetic phenomena but in the moment it's role is not completely understood. The role of alcalic ion in magnetic ordering was studied in [20].
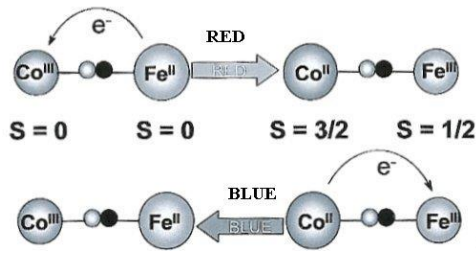

Fig.3. Reaction scheme of photo - magnetism of $KCo[Fe(CN)_6] . 6.9H_2O$ [52].

2.2. $RE[Fe(CN)_6].nH_2O$ family.

Magnetic properties and in general physical properties of rare-earth based ferricyanides has started to be subject of growing interest in seventieth of the last century, when their role in desalination of sea water was discovered. First report on the structure was made by Prandl [21] and later more precisely by Milligan [22] and Bailey [23]. Rare – earth based ferricyanides were found to crystallize in the hexagonal space group, but the removal of 1 water molecule per formula unit reduces the hexagonal symmetry to orthorombic. The Fe ions in the lattice are located along screw axes, and are octahedrally coordinated by six carbon atoms. The CN units point radially away from the central metal ion. The rare earth ions are surrounded by six nitrogen atoms at the apices of a trigonal prism and by additional H_2O molecules lying in the mirror plane opposite to the square   prism   faces, three in the hexagonal structure, but only two in the
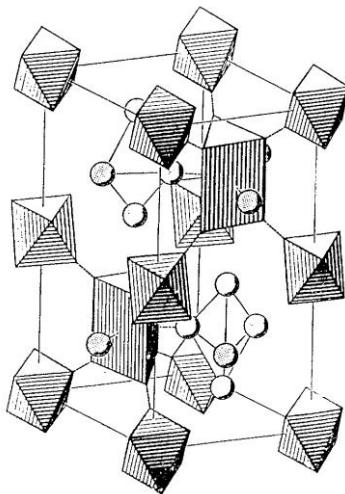
Fig.4. Hexagonal $LaFe(CN)_6 .5H_2O$ structure showing coordination of iron ions, rare earth ions and water molecules [24].
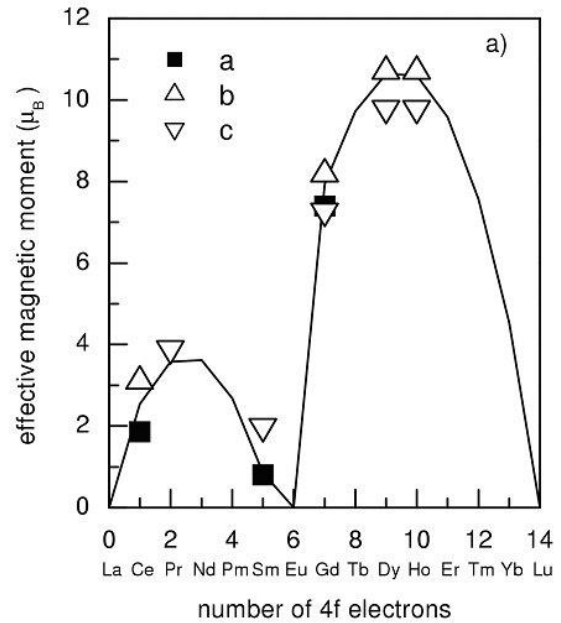
Fig.5. The influence of rare earth ion on effective magnetic moment of $RE[Fe(CN)_6]. 5 H_2O$, a and b – exerimental data, c –values for free RE ions [26].

orthorombic structure. Two   more H_2O molecules occupy holes in the structure above and below the trigonal prism faces and are obviously less strongly bonded [24].

Magnetic behaviour at low temperatures depends on both   the rare - earth and the transition elements [24-27]. Octahedral surrounding on the iron ion induces a low spin state of d electrons, the 5 d electrons of Fe(III) ion which occupy the t_{2g} triplet thus lead to an S=1/2 state . The bonding of rare – earth ion with the trigonal prismatic coordination presumably has a considerable covalent part, which is necessary for the occurence of superexchange interactions. Due to the presence of 3 different bonding angles probably both antiferomagnetic and ferromagnetic interactions are effective. This fact leads to complicated magnetic structures.   The ordering temperatures cannot simply be correlated with gJ, since the magnetic moments of most rare-earth ions are strongly anisotropic and field dependent due to the splitting of the J ground state by the electrostatic crystal field.   Some basic magnetic characteristics of rare-earth based ferricyanides are summarized in Table 1.

Experimental reports dealing with the physical characteristics of actinide-based ferricyanides have been initiated recently because it is supposed that their existence may help in nuclear waste processing (actinides separation). Synthesis and information about the structure of Np(IV), Pu(IV) and Am(III) based ferricyanides was reported in [27]. Information about synthesis and physical characteristics of Uranium U(III) and U(IV) and thorium Th(IV) based ferricyanides was reported in [28–30]. It was found   that

Table 1: Selected magnetic characteristics of rare-earth based ferricyanides $RE[Fe(CN)_6].nH_2O$. Star means invalidity of Curie-Weiss law; $T_{N,C}$ is Néel resp. Curie temperature [35].

RE	Magnetic Order	$T_{N,C}$ [K]	μ_{eff}^2 (exp.)	μ_{eff}^2 (teor)
La	antiferromagnet	(<1)	3,1	3,0
Ce	antiferromagnet	2,6	9,6	9,4
Pr	antiferromagnet	(<1)	*	*
Nd	antiferromagnet	1,9	*	*
Sm	ferrimagnet	3,5	*	*
Eu	antiferromagnet	≈ 1	*	*
Gd	ferrimagnet	3,2	67	66
Tb	metamagnet	5,7	98	97,5
Dy	ferrimagnet	2,8	114	116,3
Ho	ferrimagnet	1,3	115	115,5
Er	ferrimagnet	≈ 1	94	94,8
Tm	ferrimagnet	1,1	63	60,2
Yb	antiferromagnet	1,8	24	23,6
Lu	antiferromagnet	2,2	3,5	3,0
Y	antiferromagnet	2,0	3,2	3,0

$Th_3[Fe(CN)_6]_4.10\ H_2O$ crystallizes in cubic structure with lattice parameter a=10 Å. Due to nonmagnetic state of thorium ion, only Fe(III) ions are responsible for magnetic interactions in the lattice. $U_3[Fe(CN)_6]_4.3H_2O$ is ferromagnetically ordered bellow the temperature 4.3 K.

2.3. $A_x[B(CN)_6].nH_2O$, where A and B are 3d metals

The main stream in the research of Prussian blue analogues is however concentrated into the systems having both ion seats in the lattice occupied by the 3d ions. Some examples of this subgroup are summarized in the table 2 and table 3. Such systems are often characterized by higher values of magnetic transition temperature T_c. For example if we take as a model system $A(II)_3[Cr(III)(CN)_6]_2$, we can see that ordering temperature Tc changes from 60 K in the case of Mn(II) [31], to 240 K for Cr(II) [32], and 315 K in V(II) [33]. As we already have

Table 2 Structure and magnetic properties of $M[Mn(CN)_6]$; a [Å] - lattice constant, C [cm^{3}Kmol^{-1}], θ [Gcm^{3}mol^{-1}], M_S [Gcm^{3}mol^{-1}]-saturated magnetization, $T_{N,C}$ [K]- Néel or Curie temperature [35].

Compound	a	C	θ	M_S	$T_{N,C}$
$K_2Mn[Mn(CN)_6]$	10,15	4,9	-19	$2,50.10^4$	41
$Mn_3[Mn(CN)_6]_2.12H_2O$	10,62	16	-39	$5,50.10^4$	37
$CsMn[Mn(CN)_6].0,5H_2O$	10,69	6,2	-32	$2,08.10^4$	31
$Mn[Mn(CN)_6].1,14H_2O$	-	-	-	-	49

Table 3 Structure and magnetic properties of $M[Cr(CN)_6]$; a [Å] - lattice constant, $T_{N,C}$ [K]- Néel or Curie temperature [35].

compound	a	Mag. order	$T_{N,C}$
$CsNi[Cr(CN)_6].2H_2O$	10,57	ferromagnet	90
$V_{0,42}V_{0,58}[Cr(CN)_6]_{0,86}.2,8H_2O$	------	ferrimagnet	315
$Cr_3[Cr(CN)_6]_2.10H_2O$	------	------	240
$Cs_{0,75}Cr_{1,25}[Cr(CN)_6].5H_2O$	------	------	190
$Cr[Cr(CN)_6]_{0,5}.3H_2O$	10,37	ferrimagnet	238

mentioned earlier, the systems based on the Prussian blue are usually not free from vacancies, ions are present in the lattice in more than one oxidation state, therefore the final magnetic properties are very sensitive to exact synthesis procedure. If we will concentrate on the system with V and Cr ions in the lattice, we can see that the expected $V(II)_3[Cr(III)(CN)_6]_2$ is in reality amorphous non-stoichiometric compound, a deep-blue mixture of V(II) and V(III), $V(II)_aV(III)_{1-a}[Cr(III)(CN)_6]_{0.86}.2.8\ H_2O$ which is very sensitive to air [34]. As for this compound magnetization at saturation was very weak, coercive field is small, new syntheses were taken in order to improve its magnetic properties. A non − stoichiometric Prussian blue analogue $C(I)_aV[Cr(III)(CN)_6]_z.nH_2O$ (where C is alkali cation) with magnetic ordering temperatures varying between 295 and 330 K have been prepared [34]. How can be therefore physical properties of resultant compound modified during the process of synthesis? M.Verdaguer in [1] and [34] is suggesting the influence of the following factors:

a./ influence of (an)aerobic conditions: vanadium/chromium system prepared in aerobic conditions gives a crystalline dark green $[VO(IV)]_3[Cr(III)(CN)_6]_2$ with Curie temperature T_c=115 K. Therefore it is necessary to realize synthesis under anaerobic conditions.
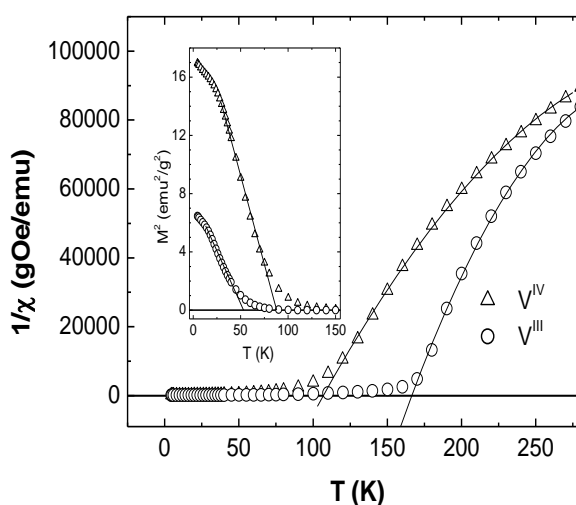
Fig.6. Plot shows the temperature of the magnetic phase transition of $(V(IV)O)_3[Cr(III)(CN)_6]_2.4H_2O$ and $V(III)[Cr(III)(CN)_6].7H_2O$ determined by two different methods [36].

b./ stoichiometry controlled by addition of countercations .

c./ nature of countercations (size, coordination)

d./ nature of the solvents .

b./, c./, and d./ points can be explained again in connection with disorder present in the lattice. Such a lattice full of vacancies and channels can accommodate a guest molecules cations (as different alcali ions for example) but also anions and solvents which can either improve or compromise the short and long range structural organization of the material. Different anions (I^-, SO^{2-}_4, Cl^-) and solvents (water, methanol, etc.) have been used in synthesis. Counterions have large effects on Tc. Disorder in the lattice can be revealed at two levels: local order (coordination of anions which decreases the number of magnetic neighbors, distortion of Cr-CN-V sequence which decreases J) and long-range order (quality of crystallization and size of the magnetic particles). The ions that do not distort the structures lead to better crystalline compounds with improved magnetic properties. Large size and weakly coordinating ions induce less disorder and favor higher values of ordering temperature T_c.
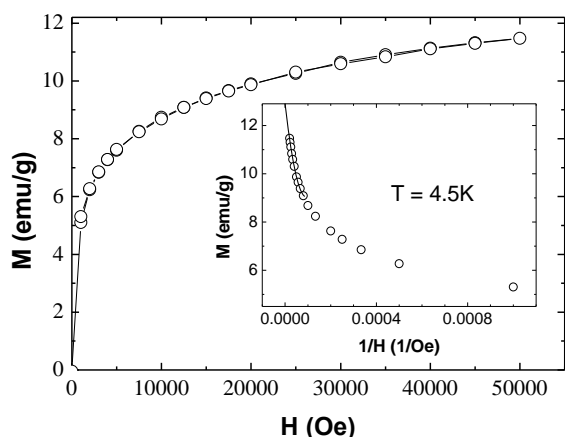
Fig.7. Magnetisation versus magnetic field measured on the sample with V(III)[Cr(III)(CN)$_6$].7H$_2$O. Inset shows a determination of the saturated magnetic moment [36].

3. APPLICATIONS

The success in obtaining Prussian blue analogues magnetically ordered at room temperature together with their unique physical properties predicts this family of materials as promising candidates for technical applications. Despite the fact that for Prussian blue analogues one cannot omit some properties, which are not favorable e.g. solubility, bad mechanical properties and low thermal stability, disadvantages are compensated by many advantages: solubility in various solvents, uniform character of the structures and the properties of the molecules, low density, optical properties (transparency), and ability to present co-functions (magnetism and optics, conductivity and magnetism).

3.1.Thin colored layers

Magnetic Prussian blue analogues display bright colors and transparency. To exploit this capability, it is useful to prepare thin films by means of electrochemical synthesis. The main technological problem connected with preparation of thin films from at room temperature magnetically ordered Prussian blue analogues is to avoid   oxidation of highly oxidisable ions such as Cr(II) and V(II) [1]. Therefore strongly negative potentials must be applied at the working electrode and the solution must be oxygen free during both the preparation as well as sample characterization. The magnetization of a transparent magnetic thin film can be tested by measuring of the Faraday effect, which corresponds to spin-dependent modifications of the transmitted light polarization.   It can be related to magnetic circular dichroism. Several authors have already reported about success in obtaining Faraday spectra on Prussian blue analogues based thin films [1, 19]. The fact that vanadium/chromium based thin films exhibit Faraday effect at a particular wavelength in the visible region leads us more close to the possibility of applications of these materials in development of new types of magneto-optical devices, e.g. opto-magnetic memory devices –by selecting specific types of laser colors, opto-magnetic multiple memory devices written by several light sources etc.

3.2.Photomagnetism

As already mentioned in section 2.1. the basic magnetic characteristics are changed when the cobalt iron polycyanide is illuminated at 5 K by the red light (500 –750 nm) . The field cooled magnetization has shown an abrupt peak at around 26 K some time (10 minutes) after illumination indicating that 3-dimensional long range magnetic ordering was established (see figure 8). The increase in T_c values is explained by an increase in the number of magnetic neighbors. The effect of illumination was demonstrated also on magnetization curves where hysteresis with remanent magnetization 3800cm^{3}mol^{-1}G and coercive field of about 6000 G at 2 K (data and Fig. taken from [19]). The change persists at 5 K for several days, when the sample was heated to 150 K the magnetic properties quickly relaxed to almost the initial state. The changes after illumination were registered also in the UV VIS, IR and Mössbauer spectra. All the changes vanish when the sample is illuminated by near IR band illumination. Such a process of illumination by visible and later near IR beam can be reversibly repeated several times showing that the magnetic properties of cobalt iron
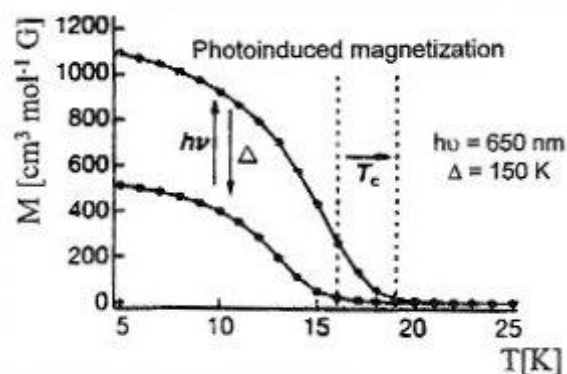
Fig.8. Photoswitching of the magnetic properties of $KCo[Fe(CN)_6].6.9H_2O$. The lower magnetization curve was measured before irradiation at 660 nm, and upper one after irradiation.

polycyanide thin films can be switched between paramagnetic and ferimagnetic state by a photo-induced electron transfer process. Reaction scheme after illumination leads from Fe(II, S=0) Co(III,S=0) to Fe(III,S=1/2),Co(II, LS, S=1/2) and to Fe(III, S=1/2), Co(II,HS, S=3/2).

It was empirically proven that a photomagnet is obtained only with the compounds whose Co and Fe ratio is from 1.4. to 1.2. The ratio of nitrogen coordination and oxygen coordination to Co depends on the stoichiometry , by which the ligand field of Co is modified. The uptake of K^+ makes possible an interaction between K^+ and the Fe-CN-Co framework. The well known cobalt-iron cyanides $Co_{1.5}[Fe(CN)_6].6H_2O$ (Co:Fe = 1.5:1) and $KCoFe(CN)_6$ (Co:Fe 1:1) do not show any photoinduced changes . For the first compound Mössbauer has shown electronic state Co(II, S=3/2) and Fe(III, S=1/2) even without illumination [19]. In the latter compound electronic state is Co(III, S=0) and Fe(II, S=0) but it is not changed after illumination. These results suggest that the energy level of Co(III)-NC- Fe(II) is situated close to that of Co(II)-NC-Fe(III) in cobalt-iron cyanide and changes by varying the ratio of Co and Fe. The energy levels can be therefore tuned by introducing defect sites in the 3-dimensional network. Large number of papers studying photoinduced changes in cobalt-iron cyanides appeared in the last years [e.g. 37-41] . In [42] the influence of alkali ion substitution is studied. $Rb_{0.66}Co_{1.25}[Fe(CN)_6].4.3 H_2O$ reveals a photo-induced long-range magnetic ordering from paramagnetic to ferimagnetic state (T_c=22 K) when irradiated at 5 K by any wavelength in the visible region due to an intense charge transfer band . The reverse process is in this case obtained only by the heat treatment. A related material which is essentially diamagnetic before irradiation (with a small amount of paramagnetic Co(II) ions) was also found to exhibit photoexcitation with T_c=21 K [43,44]. A very small effect was observed on the diamagnetic compound containing cesium cations.

The first thermally induced electron transfer leading to spin state changes close to room temperature was discovered for $Na_{0.4}Co_{1.3}[Fe(CN)_6].5H_2O$ [45]. Variation of the respective concentration of both cations leads to hysteresis effect also around room temperature [46]. Photochromic properties were also evidenced, which is appealing in terms of a possible implementation of such a kind of materials in switching devices operating at the molecular level.

A new photomagnetic effect was discovered recently on a mixed ferro-ferimagnet Fe(II)-Cr(III) cyanide derivative [47]. The temperature dependence of magnetization of $(Fe_{0.4}Mn_{0.6})_{1.5}[Cr(CN)_6].7.5H_2O$ is sum of the positive magnetization of Mn(II) sublattice and two negative magnetizations of Fe(II) and Cr(III) sublattices which have different temperature dependencies [48]. After illumination the sample with the blue light at 16 K in a weak external magnetic field (10 G), the total magnetization becomes positive , revealing a magnetic pole inversion. The pole is reversed back again by thermal treatment above 80 K. A photoinduced magnetic pole inversion , which can be induced repeatly by alternate optical and thermal stimulations , has been detected. The same strategy could be applied successfully to high T_c molecule based magnets and can lead to observation of a room temperature photoinduced magnetic dipole [47].

A growing interest was registered in Prussian blue analogues having 4d or 5d magnetic orbitals with the aim to increase interaction between the nearest magnetic neighbors and to obtain a fine-tuning of magnetic properties [49-50]. Some of such materials show also photomagnetic effects [51].

REFERENCES

[1] Anonymous, Miscellanea Berolinensia ad incrementum scientiarum (Berlin) 1 (1710) 377

[2] M.Verdaguer, A.Bleuzen, V.Marvaud et al, Coordination Chemistry Reviews, Vol. 190-192, (1999), p.1023-1047

[3] H.J.Buser, A.Ludi, W.Petter, D. Schwarzenbach,J.Chem.Soc.Chem.Commun. (1972),p.1299

[4] J.F.Keggin,F.D.Miles, Nature , 137, (1936),p.577

[5] A.Ludi, H.U.Güdel, Struct.bonding 14, (1973), p.1

[6] M.R.Robin, Inorg.Chem.,1, (1970), p.337

[7] F.Herren, P.Fischer, A.Ludi, W.Hälg, 19, Inorg. Chem.(1980), p.956

[8] J.B.Goodenough, Phys. Rev.100(1959), p.564

[9] J.B.Goodenough, J.Phys.Chem.Solids, 6,(1958),p.287

[10] J.Kanamori,J.Phys.Chem.Solids, 10(1959),p.87

[11] A.P.Ginsberg,Inorg.Chim.Acta.Rev.,5(1971),p. 45

[12] M.Nishino, S.Kubo, Y.Yoshioka,et al, Mol.Cryst.Liq.Cryst.305(1997), p.109

[13] Pharr, C.M., Griffiths, P.R., Anal. Chem. 1997, 69, 4673-4679

[14] K.Yoshizawa, F.Mohri, G.Nuspl, T.Yamabe, J.Phys.Chem.B, 102 (1998), p.5432

[15] M.Zentková, M.Broschová, M.Mihalik, J.Rusz, Proceedings of the 6-th international workshop Applied Physics of Condensed Matter, Kočovce (2000), p.100

[16] T.Wasiutynski, Z.Szeglowski, A.W.Pacyna, M.Balanda, Physica B, 253 (1998), p.305

[17] O.Sato, T.Iyoda, A.Fujishima , K. Hashimoto, Science, 272, 3May 1996, p.704

[18] P.Gütlich, Y.Garcia, T.Woike,Coordination Chemistry Reviews, 219-221, (2001), p.839

[19] S. Ohkoshi, K. Hashimoto, J. Photochem. And Photobiology C: Photochemistry Reviews, 2 (2001), p.71

[20] T. Wasiutynski, M.Balanda, Z.Szeglowski, P.M.Zielinski, Polish J. Chem. , 76, (2002), p.377

[21] W.Prandtl, S.Mohr, Z.Anorg.Allgem.Chem. 236,(1938), p.243

[22] W.O.Milligan, M.Uda, R.D.Dillin et al, Research and Develop.Progr. No.723, Int-OSW-RDPR-71-723, US Dept. Of Interior (October 19710.

[23] W.E.Bailey, R.J.Williams, W.O.Milligan, Acta Crystallogr. B29, (1973),p.1365

[24] F.Hulliger, M.Landolt, H.Vetsch, J.Solid State Chemistry, 18(1976),p.283

[25] M.Zentková, A.Zentko, I.Žežula, acta physica slovaca, vol. 48, (1998), No.6., p.837

[26] V.Kavečanský, J.Kováč,M.Zentková, I.Žežula, Czech.J.Phys., Vol.52,(2002),p.333

[27] I.Bonhoure, Ch. Den Auwer et al, 29[iemes] Journees des Actinides ,14-17 May 1999, Luso, Portugal, Book of Abstracts , p.12

[28] M.Zentková, R.Göbl, M.Maryško, A.Zentko, Phys.Stat.Sol. (a), 172(1999),R1

[29] R.Göbl, A.Zentko, et al, Czech.J.Phys., 50, (2000), p.671

[30] R.Göbl, M.Zentková, V.Kavečanský et al, acta physica polonica A, 97(2000),No.5.,p.835

[31] O.Kahn, Nature,378(1995),p.677

[32] T.Mallah, S.Thiebaut, M.Verdaguer, P.Veillet,Science, 262, (1993),p.1554

[33] S.Ferlay, T.Mallah, R.Ouahes et al, Nature 378, (1995), p.701

[34] M.Verdaguer, A.Bleuzen, C.Train et al, Phil.Trans.Soc.Lond.A, 357, (1999), p.2959

[35] M. Lukáčová: "Magnetizmus vybraných magnetov obsahujúcich 3d- a 4f- prvok", písomná práca k dizertačnej skúške (2002).

[36] M. Lukáčová, L.F. Kiss, M. Maryško, M. Mihalik, Z. Mitróová, J. Stopka, A. Zentko, M. Zentková: "New Magnetic Phenomena in Vanadium Hexacyanochromates", accepted in phys. stat. sol.

[37] A.Goujon, O.Roubeau, F.Varret, A.Dolbecq, A.Bleuzen, M.Verdaguer, Eur.Phys.J B14, (2000), p.115

[38] D.A.Pejakovic, J.L.Manson, J.S.Miller, A.J.Epstein, J.Appl.Phys. 87, (2000), p.6028

[39] D.A.Pejakovic, J.L.Manson, J.S.Miller, A.J.Epstein, Phys. Rev. Lett. 85 (2000), p.1994

[40] M.Nishino, K.Yamaguchi, S.Miyashita, Phys.Rev.B, 58 (1998), p.9303

[41] T.Kawamoto, Y.Asai, S.Abe, Phys. Rev.Lett.86 (2001), p.348

[42] O.Sato, Y.Einags, A.Fujishima, K.Hashimoto, Inorg.Chem.38 (1999), p.4405

[43] A.Bleuzen, C.Lomenech, A.Dolbecq, F.Villain, A.Goujon et al, Mol.Cryst.Liq.Cryst.335 (1999), p.253

[44] C.Cartier, F.Villain, A.Bleuzen, M.A.Arrio et al, J.Am.Chem.Soc.122 (2000), p.6653

[45] O.Sato, Y.Einaga, A.Fujishima, K.Hashimoto, J.Phys.Chem.B 101, (1997), p.3903

[46] N.Shimamoto, S.Ohkoshi, O.Sato, K.Hashimoto, Mol.Cryst.Liq.Cryst., 344 (2000), p.95

[47] S.Ohkoshi, K.Hashimoto, J.Am.Chem.Soc. 121 (19990, P.10591

[48] S.Ohkoshi,Y.Einaga,,A.Fujishima, K.Hashimoto, J.Electroanal.Chem. 473 (1999), p.245

[49] J.Larionova, M.Gross, M.Pilkington et al, Angew.Chem.Int.Ed.Engl. ,39 (2000), p.1605

[50] Z.J.Zhong, H.Seino, Y.Mizobe, M.Hidai, M.Verdaguer, S.Ohkoshi, K.Hashimoto, Inorg.Chem. 39, (2000), p.5095

[51] G.Rombaut, S.Golhen, L.Ouahab, C.Mathoniere, O.Kahn, J.Chem.Soc.Dalton Trans. (2000), P.3609

[52] M.Verdaguer, Science 272, (1996), p.698

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