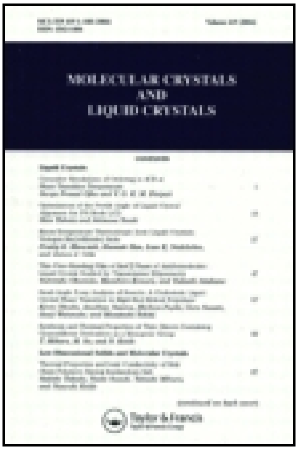

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Magnetism in Low-Dimensional Cr(II) and Fe(II) Organophosphonates

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Magnetism in Low-Dimensional Cr(II) and Fe(II) Organophosphonates

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The synthesis and the magnetic characterization of new layered compounds of formula $Cr[NH_3(CH_2)_2PO_3(Cl)]$, $Fe[C_6H_5PO_3]\cdot H_2O$ and $Fe_2[O_3P\text{-}(CH_2)_2\text{-}PO_3]\cdot 2H_2O$ is presented. The compounds order antiferromagnetically at the critical temperature T_N, which is at 4.9K for the first one, at 21.5K for the second and at 24K for the third one. Below T_N, they all behave as a *weak ferromagnet.*

Keywords: metal(II) phosphonates; weak ferromagnets

INTRODUCTION.

Hybrid layered compounds, consisting of alternating inorganic and organic layers, have provided interesting examples of low-dimensional magnetic materials.[1] Typical materials having this type of crystal structure are the "*intercalation*"[2] and "*molecular composite*"[3] compounds. In contrast with intercalation compounds, which can exist both with and without organic molecules between layers of the lattice, in molecular composite solids, the organic groups are covalently or ionically bound to the inorganic layers. Examples of the latter are represented by the layered perovskite halides $(RNH_3)_2[MX_4]$, (R=alkyl or aryl group, M=divalent metal ion, X=halogen), [4,5] and by the metal organophosphonates.[6] Such materials provide an opportunity for tailoring new and functional materials for basic science and technological applications. For the above mentioned reasons, we have undertaken a study on the synthesis and the physical properties of 1st series transition metal(II) phosphonates. This widespread group of salts has the general formula $M[C_nH_{2n+1}PO_3]\cdot H_2O$ and $M_2[O_3P\text{-}(CH_2)_n\text{-}$

$PO_3]\cdot 2H_2O$, (M=Mg,Cd,Cu,Mn,., n=1,2,..) and, in the most common crystal structure, the metal ions are bridged by the oxygens of the phosphonate ligands and they form sheets that are separated one from the other by the organic substituents of the ligands. The two-dimensional nature of this lattice favours the next-neighbours exchange magnetic interactions in phosphonates containing paramagnetic ions and, at low temperatures, a long-range magnetic ordering is often observed. Recent studies on the magnetic properties of $M[C_nH_{2n+1}PO_3]\cdot H_2O$, M=Mn(II), Fe(II), Cr(II),[7-11] have shown the compounds order antiferromagnetically at low temperatures. But, below the ordering temperature, T_N, the equilibrium distribution of moments is not as collinear, as should be expected, but canted from the magnetic easy axis, giving rise to a spontaneous magnetization. The existence of the hysteresis loop, below the critical temperature, confers a memory effect on the material. This phenomenon is known as *canted antiferromagnetism* or *weak ferromagnetism*, and it was observed for the first time in α-Fe_2O_3.[12] In this paper the synthesis, the structural and magnetic studies of a new series of molecule-based weak ferromagnetic materials of the Fe(II) and Cr(II) phosphonates is presented and discussed.

RESULTS

The phosphonic acids were prepared by the Michelis–Arbuzov method,[13] or purchased from Aldrich Chem. Co, and used as delivered. In general the preparation of metal(II) phosphonates requires the deprotonation of the ligand and the reaction was always carried out, expecially for diamagnetic metal ions, such as Zn, Cd, Mg, in the presence of NaOH in water. In the case of Cr(II) and Fe(II) the pH required for the deprotonation favours the formation of metal hydroxides and therefore preventing the isolation of the phosphonates. The reaction between the metal ion salt and the phosponic acid was then carried out in the presence of urea, by refluxing for a few days the mixture at 80°C under N_2 gas, to avoid the oxidation of the metal ions. The compounds were isolated as a polycrystalline powder.[10,11]

CRYSTAL STRUCTURES

The crystal structures of the metal(II) phosphonates reported in this paper have not yet been solved, except that of $Fe[C_6H_5PO_3]\cdot H_2O$.[14] In this compound the iron(II) is six-coordinated by five oxygen atoms of the ligand and the sixth position is occupied by the water molecule.

Since in the formula there is only one ligand, in order to obtain octahedral coordination, two of the phosphonate oxygens chelate the metal and, at the same time, bridge across adjacent metal atoms in the same row; these oxygens are therefore three-coordinate. This arrangement produces a correlated or kinked layer, perpendicular to which are located the phenyl groups oriented in a disordered way. The organic groups form bilayers between two adjacent inorganic ones.

MAGNETIC PROPERTIES

$Cr[NH_3(CH_2)_2PO_3(Cl)]$.

The inverse of static molar magnetic susceptibility has been measured in the temperature range 1.8÷300K by using a SQUID Quantum Design MPS5 magnetometer. From 20K to room temperature the magnetic behavior is typical of a paramagnetic system and in accordance with the Curie-Weiss law, the Curie constant, C, being 2.496 emu·K·mol^{-1}, and the value of the Weiss constant, θ=-1.2K, as fitted to the high temperature susceptibility data. The value of C corresponds to an effective magnetic moment of $4.7\mu_B$, and it is consistent with the presence of Cr(II) ion, in the d^4 (S=2) high-spin configuration. On cooling down the sample, the product χ*T starts to increase at T=6K and a peak is observed at T=4.9K. Field-cooled magnetization (*FCM*) and the zero-field-cooled (*ZFM*) magnetization at the applied field of 100mT, in the temperature range of 2÷15K, were then measured (see Figure 1). The *FC* magnetization, obtained on cooling the sample within a field of 100G, shows a rapid increase at T=4.9K. The *ZFC* magnetization, obtained on cooling the sample in zero field and then warming it in the same field, shows a narrow peak at T_N ~5K. The difference between *FCM* and *ZFCM* represents the remnant magnetization, M_{remn}, induced in cooling within a field below the critical temperature and switching off the field. The remnant magnetization disappears upon warming at T = 4.9K, taken as the critical temperature, T_N.

$Fe[C_6H_5PO_3]\cdot H_2O$.

The d.c. static magnetic susceptibility measurements were performed on a polycrystalline sample in the temperature range 6÷270K and in an applied field of 50mT. Above 80K, the inverse of molar magnetic susceptibility, $1/\chi_M$ vs T is linear, according to the Curie-Weiss law, and the Curie constant, C, is 3.15emu·K·mol^{-1}, as fitted to the high temperature susceptibility data by using the equation $\chi=C/(T-\theta)$. This corresponds to an

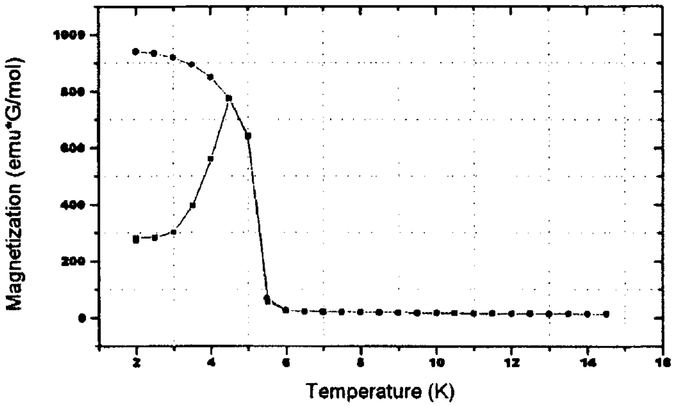

FIGURE 1. Temperature dependence of the z.f.c. (■■■) and f.c (• • •) magnetization of $Cr[H_3N\text{-}(CH_2)_2\text{-}PO_3(Cl)]$ below 10K.

effective magnetic moment $\mu_{eff}=5.0\mu_B$, consistent with the presence of Fe(II) in a d^6 high-spin electronic configuration. The Weiss constant, *i.e.* $\theta=-56K$, is negative and high in absolute value, thus indicating strong antiferromagnetic near-neighbour exchange interactions between the adjacent iron(II) ions. Below 100K the product χ*T vs T slightly decreases and then it rises again to a maximum at T= 21K. Field-cooled , the zero-field-cooled and remnant magnetizations in the 6÷25K temperature range are reported in Figure 2. The *ZFC* magnetization shows a broad peak centered at T~21K. The *FC* magnetization shows a rapid increase at T = 23K and then it starts to be constant at T ~13K down to the lowest measured T=6K. The difference between *FCM* and *ZFCM*, *i.e.* the remnant magnetization, M_{remn}, disappears upon warming at the critical temperature, T_N=21.5K. Isothermal magnetization as a function of magnetic field was measured at T=10K, a temperature well below the critical temperature. It reaches the value of ~1,700 emu*G/mol at 4 Tesla, and this value is ~ 7% of that expected for an S=2 system. Hysteresis loops at T=10K and at T=21K were also measured. The plot at T=10K shows that the values of the coercive field, H_c, and of the remnant magnetization, M_{remn}, are 6,400G and 740 emu•G/mol, respectively. The hysteresis loop, measured near the critical temperature, *i.e.* T=21K, shows

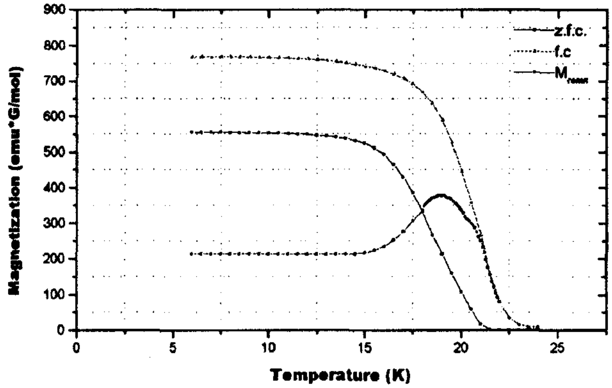

FIGURE 2. Temperature dependence of the z.f.c., f.c. and remnant magnetization of $Fe[C_6H_5PO_3]\cdot H_2O$ below 25K.

where M_{nc} is the uncompensated (weak ferromagnetic) moment, and χ_{AFM} is the antiferromagnetic susceptibility. M_{nc} was determined from the extrapolation to zero field of the linear part of the magnetization curve at high applied magnetic fields and χ_{AFM} was determined as its slope. The values were found to be 550emuG/mol and 0.029emu/mol, respectively. Hysteresis phenomena disappear at temperatures above T_N, where the isothermal magnetization vs field plot is linear.

$Fe_2[O_3P\text{-}(CH_2)_2\text{-}PO_3]\cdot 2H_2O$.

Static magnetic susceptibility measurements were made on a polycrystalline sample of $Fe_2[O_3P\text{-}(CH_2)_2\text{-}PO_3]\cdot 2H_2O$, in the temperature range 5÷270K . The sample was zero-field cooled to 5K and the magnetization measured on heating the sample to 270K. The temperature dependence of the reciprocal of the molar magnetic susceptibility, $1/\chi$, is linear above 100K. The Curie constant, C, is 6.844 emu·K·mol^{-1}, as fitted to the high temperature susceptibility data by using the equation $\chi = C/(T-\theta)$, and this corresponds to an effective magnetic moment of $5.24\mu_B$, consistent with the presence of Fe(II) in a d^6(S=2) high-spin configuration. This value is slightly higher than that expected for the spin-only moment, *i.e.* 4.9μ_B. The $^5D(L=2)$ free-ion state of Fe(II) ion has orbital degeneracy, and, in a cubic ligand field, the ground state is $^5T_{2g}$ ground state, with the lowest spin-orbit state J=1.[16] An introduction of a distortion in the $[FeO_6]$ site by the ligands causes a further splitting of the J=1 state, and the resulting ground state can be either a singlet , Mj=0, or doublet , Mj=±1. Because the energy separation between the spin-orbit components in Fe(II) is of the order of 200cm^{-1}, so we expect an orbital contribution to the Fe(II) moment, which could explain the observed difference. The large negative value of Weiss constant, *i.e.* θ=-55K, indicates strong antiferromagnetic *near*-neighbour exchange between the adjacent iron (II) ions. Deviation from Curie-Weiss occurs below 80K . The χ*T vs T shows in fact a peak at T≅24K. This peak can be associated to a *three*-dimensional antiferromagnetic ordering, T_N. The *FC* magnetization and the *ZFC* magnetization in the 5÷30K temperature range were measured. The *FCM* shows a rapid increase at T= 24K and the *ZFCM* shows a peak at T_N ~23K. The remnant magnetization, M_{remn}, disappears upon warming at T_N=24.5K. This temperature is taken as the critical temperature, T_N . The magnetic hysteresis loop at T=20K was also measured, and the value of the coercive field, H_r, is 1000Oe and the remnant magnetization, M_{remn}, is 750emu·G/mol. The latter value is ≈4% of the saturation value expected from an S=2 spin system, as calculated from the relation: $M_s=Ng\mu_B S$, where N is the Avogadro's number. This corresponds then to the saturation of weak ferromagnetic moments. Hysteresis phenomena disappear at temperatures above T_N. At T=30K, and, in fact the isothermal magnetization *vs* field plot is linear.

CONCLUDING REMARKS

Molecule-based "weak" ferromagnets are uncommon. Typical examples include $Mn(RPO_3)H_2O$, R=alkyl group,[8,9] $(NH_4)M^{II}PO_4$, M=Mn,Fe,[17] $M[N(CN)_2]_2$, M=Cr,Mn[18] and they are the third category of magnetic solids, with a finite zero-field spontaneous magnetization below a certain ordering temperature. The compounds reported in this paper are new and they order antiferromagnetically at critical temperatures, which are found to be around 24K for the Fe(II)phosphonates and T_N=4.9K for $Cr[NH_3(CH_2)_2PO_3(Cl)]$. The antiferromagnetism in the case of iron(II) salts arises from interactions between nearest neighboring ions, that take place *via* two different 180° Fe-O-Fe superexchange paths. The magnetic parameters of the iron(II) phosphonates are reported in Table 1. The purely inorganic $(NH_4)Fe^{II}PO_4\cdot H_2O$ has also been included, because it possesses the same metal-oxygen-phosphorus layer and because it is a "canted" antiferromagnet.[17] The NH_4^+ ion lies in the interlayer region and the organic phosphonic groups are replaced by the phosphate oxygen. In this series the inorganic Fe(II) phosphate and the two Fe(II) organo-phosphonates show the same values for the critical temperature, T_N, while in $Fe(C_6H_5PO_3)H_2O$ is slightly lower. The critical temperature along the series is nearly constant and it seems to be independent of the distance between the inorganic layers.

TABLE 1. Magnetic parameters of Fe(II) phosphonates.

Compound	T_N (K)	θ (K)	T_N/θ	Space group	interlayer distance (Å)
$(NH_4)FePO_4\,H_2O$	24.0	-65	0.37	$Pmn2_1$	8.8213(2)
$Fe(C_2H_5PO_3)H_2O$	24.5	-43	0.57	P1n1	10.33(1)
$Fe(C_6H_5PO_3)H_2O$	21.5	-56	0.38	$Pmn2_1$	14.453(2)
$Fe_2[O_3P(CH_2)_2PO_3]\cdot 2H_2O$	24.0	-55	0.44		15.23

Below these temperatures, the magnetic behavior of the compounds is characteristic of a “*weak ferromagnet*”or “*canted*“ antiferromagnet. The observed weak ferromagnetism is due to the spin canting.[12] The local spins in the ordered magnetic state then are not perfectly antiparallel, which results in an uncompensated resultant moment in one direction. The spin canting is indicative of the low symmetry of the ligand field around the open-shell metal ion, because only in this situation the so-called antisymmetric exchange [12b] may occur between neighbouring centeres and compete with collinear antiferromagnetism.

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