Crystallographic and magnetic studies of the mixed pyrophosphates $AMnP_2O_7$, A ≡ Co, Ni, Cu

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Abstract

The pyrophosphate $A^{II}Mn^{II}P_2O_7$ with A ≡ Co, Ni, Cu was prepared. The three phases have the structure $Mn_2P_2O_7$. Preliminary magnetic measurements were taken. The magnetic behaviour was found to be typical of ferrimagnetic chains coupled antiferromagnetically at a low temperature.

1. Introduction

Over the past ten years a number of structural resolutions have been performed on the mixed pyrophosphates $A^{II}B^{II}P_2O_7$ where A is an alkaline earth and B a transition element. We have pointed out that depending on the size of A, the ion B^{II} occupies either an octahedral or pyramidal environments, and that the groups B_2O_{10} are divided into either sheets or cages. Thus for A ≡ B in the compounds $BaCoP_2O_7$, $BaNiP_2O_7$ [1] and $BaCdP_2O_7$ [2], the structure is composed of sheets, while for A ≡ Ca the structure forms cages in the compounds $CaCoP_2O_7$ [3] and layers in $CaCuP_2O_7$ [4]. The former sheet is found where A ≡ Sr or Mg in the compounds $SrCdP_2O_7$ [2] and $(Mg_xCo_{1-x})P_2O_7$[5].

It should be noted that with the exception of the compounds $CaCuP_2O_7$ and $(Mg_xCo_{1-x})P_2O_7$ where the copper and cobalt provide a pyramidal environment, in diphosphates the transition element is located in an octahedral environment.

As a logical progression of our crystallographic and magnetic investigation of the compounds $CoNiP_2O_7$, $CoCuP_2O_7$ and $NiCuP_2O_7$ [6], and in order to stabilize two magnetic sublattices with a non-zero moment, we prepared a series of products with the form $AMnP_2O_7$ with A ≡ Co, Ni or Cu. In these compounds the common ion is Mn^{II} with high spin $S = 5/2$.

2. Synthesis

The samples were prepared as powders, following three different methods.

Solid. In this method a mixture in stoichiometric proportions of oxides or carbonates of a transition element, and of diammonic hydrogenophosphate was prepared. The mixture was finely ground and brought gradually to 900 °C.

Coprecipitation. When mixing the transition element solution of nitrates or sulphates with the tetrasodic pyrophosphate solution, we obtain a precipitate that gives the desired pyrophosphate after several rinses in water, followed by calcination at 600 °C.

Sol–gel. The molar concentration of orthophosphoric acid is twice than that of the transition element of the chloride solutions. The gel obtained between pH 4.5 and 9.5 is brought to 100 °C and then to 500 °C.

The advantage of these last two methods is that at the microscopic level they produce a homogeneous powder composed of smaller grains, this helps agglomeration and brings about calcination at a lower temperature.

3. Characterization by IR spectroscopy and X-ray diffraction

3.1. IR spectroscopy

The IR absorption spectra were recorded using a Nicolet 5DXC spectrometer. The samples were ground

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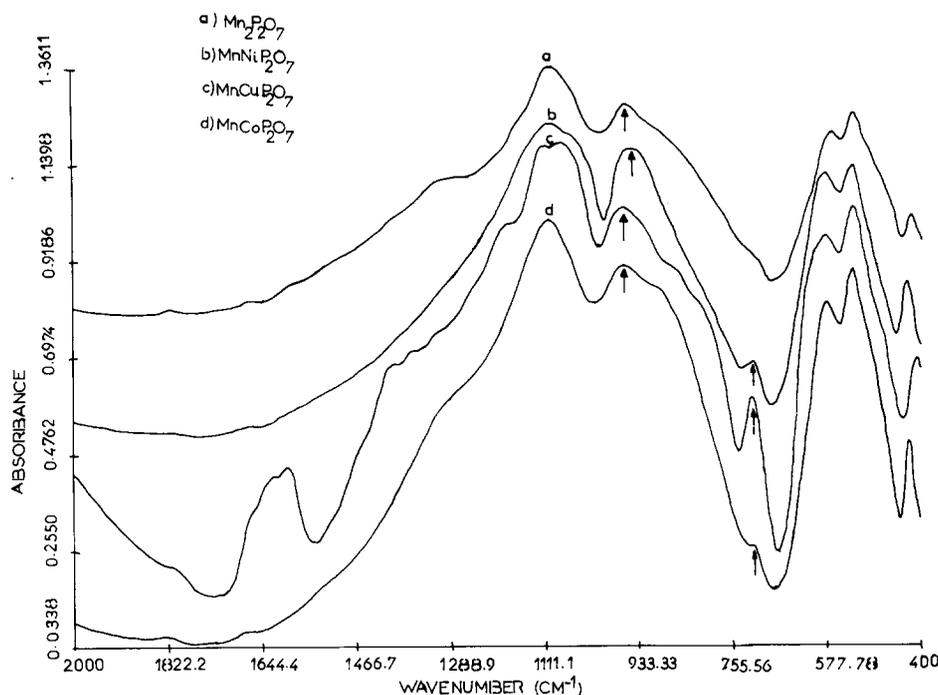
Fig. 1. Representative IR spectra of pyrophosphates $MnCoP_2O_7$, $MnCuP_2O_7$ and $MnNiP_2O_7$.

in previously desiccated KBr powder. The group P_2O_7 is easily identified by the following absorption bands [7]: a group of bands of greater or lesser complexity centred around $1100\,cm^{-1}$ and attributed to the antisymmetrical vibration of the outer groups PO_3; a strong band of varying width in the region $950-900\,cm^{-1}$ produced by antisymmetrical vibration of the bridge P–O–P; a weak band (sometimes a doublet) in the region $750\,cm^{-1}$ attributed to the symmetrical vibration of P–O–P.

We may note that this last band distinguishes a pyrophosphate from an orthophosphate. In fact, the group PO_4 does not show any vibrational frequencies in the region around $750\,cm^{-1}$. However, the absence of this band in $Mn_2P_2O_7$ (Fig. 1) is attributed to the linear nature of the P–O–P bridge in this compound.

3.2. X-ray diffraction

The diffraction patterns of the compounds in powder form were recorded on a Philips diffractometer fitted with an iron anticathode ($\lambda Fe\,K\alpha = 1.937\,\text{Å}$).

The diffraction patterns show that the phases $MnCoP_2O_7$, $MnCuP_2O_7$ and $MnNiP_2O_7$ are isostructural and may be related to $Mn_2P_2O_7$, crystallizing in the monoclinic system and the space group $C_{2/m}$ [8]. Cell dimensions, after the least squares refinement, are given in Table 1.

4. Magnetic studies

The magnetic experiments were carried out using a DSM8 magnetometer (Echics, Strasbourg) based on the Faraday method, in the temperature range 4–300 K and for $H = 14\,kG$. The measurements are given with signal accuracy of $2 \times 10^{-5}\,emu\,mol^{-1}$ and 0.1 K for the temperature. $\chi(T)$ values are corrected for diamagnetic and Van Vleck contributions [9, 10].

The experimental data (Fig. 2) of the [MnCo] compound exhibits a typical maximum of an antiferromagnetic transition at $T < 10$ K. In contrast, $\chi(T)$ shows a plateau at a very low temperature for the [MnCu] and [MnNi] compounds. At high temperature, Curie–Weiss behaviour is observed with θ_p values ranging from -3 to -6 K. The magnetic data are listed in Table 2 with ratios of cell dimensions.

The theoretical values of C given in Table 2 correspond to spin only values. So, the discrepancy observed in the case of [MnCo] is related to the well known orbital effect for the Co(II) ion. In this case, the decrease in $\chi(T)$ from room temperature to around 20 K is due to the spin-orbit coupling effect.

It is to be noticed that the variation of $\chi(T)$ for [MnCu] is quite typical of ferrimagnetic behaviour. The minimum of $\chi(T)$ is well known for 1d ferrimagnets [10, 11]. Below 10 K, the fall in $\chi(T)$ is probably related to antiferromagnetic long-range ordering.

TABLE 1. Cell dimensions

	Compound			
	$MnCoP_2O_7$	$MnNiP_2O_7$	$MnCuP_2O_7$	$Mn_2P_2O_7$ [8]
a (Å)	6.533(7)	6.560(4)	6.604(4)	6.633(1)
b (Å)	8.664(5)	8.543(5)	8.643(7)	8.584(1)
c (Å)	4.548(4)	4.515(3)	4.557(1)	4.546(1)
β (deg)	101.70(1)	101.29(3)	102.23(1)	102.67(1)
V (Å^3)	252.37	248.21	254.25	252.6
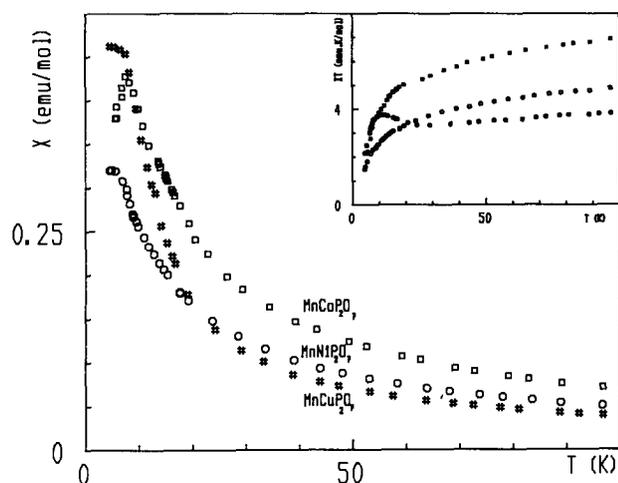
Fig. 2. Temperature dependence of magnetic susceptibility χ and $\chi(T)$ product of the compounds $MnCoP_2O_7$, $MnCuP_2O_7$ and $MnNiP_2O_7$.
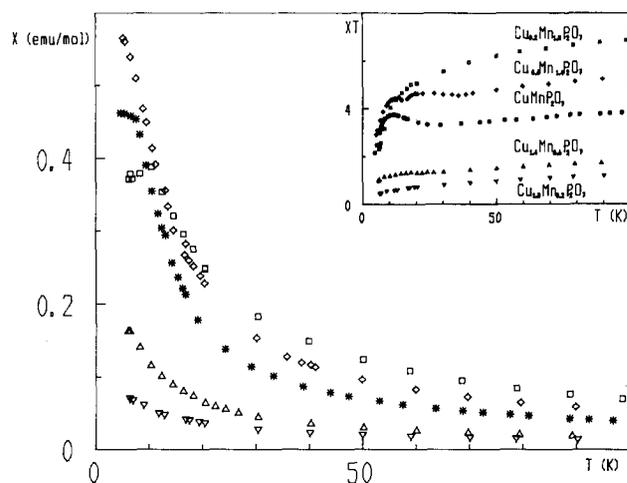
Fig. 3. Temperature dependence of χ and $\chi(T)$ of solid solutions of $(Mn,Cu)P_2O_7$.

Similar behaviour is observed for the mixed systems $(Mn, Cu)P_2O_7$ for 42%–50% copper (Fig. 3).

5. Discussion

The decrease in $\chi(T)$ observed at low temperatures for the systems under consideration agrees with the presence of significant antiferromagnetic interactions.

In fact, two regimes may be emphasized. In the paramagnetic region (above T_c), the systems behave as quasi isolated chains, in agreement with structural findings [8]. Depending on the amount of order between both kinds of metal ions, the chains exhibit either antiferromagnetic behaviour ([MnNi],[MnCo]) or ferrimagentic behaviour ([MnCu]). Then, at low temperature, an antiferromagnetic ordering between these chains is stabilized, leading to a decay in the $\chi(T)$ product.

It may be noted that the ferrimagnetic 1d behaviour observed for [MnCu] is similar to that reported in EDTA complexes [12–14]. It was shown that 1d ferri-

magnetism is stabilized when two different magnetic sublattices are present. These can arise from alternating metal ions or alternating Landé factors in relation to different environments.

Further, ferrimagnetic-like behaviour has recently been reported for some exotic chains with competing exchange interactions [15–18].

6. Conclusions

Crystallochemical investigation of the compounds in powder form has shown that the pyrophosphates $MnCoP_2O_7$, $MnNiP_2O_7$ and $MnCuP_2O_7$ may be related to $Mn_2P_2O_7$ crystallizing in the monoclinic system and the spatial group $C_{2/m}$ [8]. These results will be supplemented by crystallographic investigation of the monocrystalline form.

We have also tried to characterize the magnetic behaviour of these compounds by referring to previous studies carried out on $MM'(EDTA) \cdot 6H_2O$.

TABLE 2. Magnetic data

	Compound				
	$MnCoP_2O_7$	$MnNiP_2O_7$	$MnCuP_2O_7$	$MnZnP_2O_7$[a]	$Mn_2P_2O_7$
a/b	0.7541	0.7679	0.7641	0.7727	0.7727 [8]
c/b	0.5249	0.5285	0.5272	0.5280	0.5296 [8]
c/a	0.6961	0.6884	0.6900	0.6838	0.6854 [8]
T_N (K)	8	5	10[b]	8.5	12
C_{obs} (emu K mol^{-1})	6.9	5.2	4.3	3.9	8.8
C_{the}[c] (emu K mol^{-1})	6.3	5.4	4.8	4.4	8.75
θ_p[d] (K)	−4.1	−5.8	−3.2	−3	−12

[a]Data to be published.
[b]Ferrimagnetic order temperature.
[c]The values of Curie constant correspond to two transition elements with oxidation degree +2 and Landé factor $g = 2.1$.
[d]$\chi = C/T - \theta_p$ for $T \geq 10\theta_p$.

While the behaviour of the compounds $MnCoP_2O_7$ and $MnNiP_2O_7$ is antiferromagnetic, for $MnCuP_2O_7$ the variation in the product $\chi(T)$ suggests behaviour characteristic of ferrimagnetic chains, coupled antiferromagnetically at low temperature (around 10 K).

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