# Magnetic properties of $M_2P_4O_{12}$ ( M = Ni, Co, Cu)

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We have discussed thermodynamic properties from susceptibilities and specific heat mesurements of isostructural one-dimensional $M_2P_4O_{12}$ system. The compounds show different magnetic behaviours, varied from ferromagnetic to antiferromagnetic ordering.

## I. Introduction

Within the context of low dimensional systems studies[1-3], several magnetic compounds have received a great attention in research these last three decades, as is the case of the systems reported here namely $M_2P_4O_{12}$. Where M stand for divalent transition metals (M = Cu, Co, Ni). Our interest in this paper is to determine their thermodynamic properties. The correlation between the structural and magnetic properties is olso discussed.

## II.Structural description

The compounds belong to a group of isostructural $M_2P_4O_{12}$ with monoclinic C2/c space group symetry[4-7]. The cell parameters of the titled compounds are listed in table 1. Their crystal structure is built up of two distinct $MO_6$ octahedron, known by $M_I$ and $M_{II}$ sites, linked by edge-sharing forming a zig zag chain like $M_IO_6$-$M_{II}O_6$-$M_IO_6$-$M_{II}O_6$ along $(10\bar{1})$ direction (figure 1,a). The closed distance between magnetic ions in chains of each compound is uniform. The magnetic chains are separated by $P_4O_{12}$ groups as shown in figure 1,b.

| | a(A°) | b(A°) | c(A°) | β | Ref. |
|---|---|---|---|---|---|
| $Cu_2P_4O_{12}$ | 12.56 | 8.088 | 9.574 | 118.58 | 4 |
| $Co_2P_4O_{12}$ | 11.809 | 8.297 | 9.923 | 118.72 | 6 |
| $Ni_2P_4O_{12}$ | 11.65 | 8.241 | 9.857 | 118.46 | 5 |

Table1: Cell parameters of $M_2P_4O_{12}$ (M = Cu, Co, Ni)

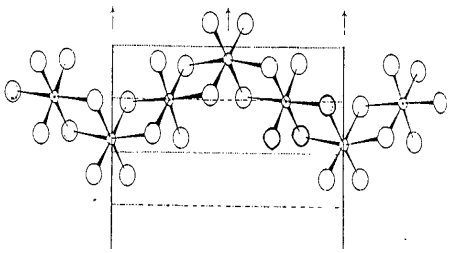

Figure 1,a: Projection of a chain of cations on the $(10\bar{1})$ plane (after ref. 4)

Due to the Jahn teller effect, the $CuO_6$ in $Cu_2P_4O_{12}$ are very distorted compared with $NiO_6$ and $CoO_6$ octahedron. So this will have extreme consequences for the magnetic behaviours.

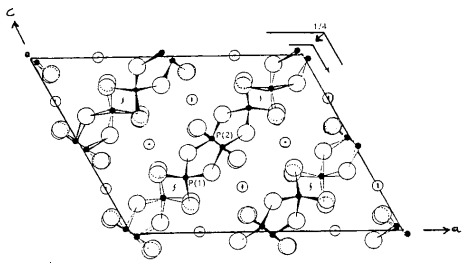

Figure 1,b: Projection of $M_2P_4O_{12}$ on (010) plane (after ref. 4) ○ M • P ○ O

## III.Magnetic properties

Let us now examine the magnetic behaviours of each compound through a plot of both susceptibility and magnetic moment vs. temperture.

At high temperture, the reciprocal susceptibility of $Ni_2P_4O_{12}$ follows the Curie-Weiss law,

 

$\chi$ = C/T- $\theta$, with C = 2.44 (emu.K.mol$^{-1}$) and $\theta$ = 5.8 K. From the positive value of paramagnetic temperture, ferromagnetic intrachain interaction anticipated. The magnetic moment found from Curie constant is 3.12$\mu_B$ per atom. The variation of the susceptbility with temperture in figure 2 shows a sharp maximum at T = 14 K, caracteristic of an antiferromagnetic tridimensional phase transition. In the same figure, we plotted the temperature dependence of effective magnetic moment. It exhibits a maximum at 18 K, separate the behaviour into two different regimes. At high temperture, the behaviour is similar to a ferromagnetic quasi-isolated chain. Below 18 K, antiferromagnetic interchain interaction becomes more important, thus the magnetic moment feature fall brutally.

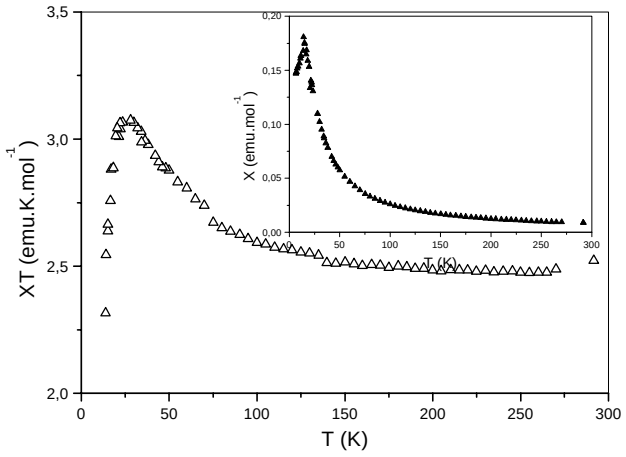


Figure 2 : Variations of the product $\chi$T and susceptibility (in insert) vs. temperature of $Ni_2P_4O_{12}$ powder.

With the mean field approximation, we can estimate the intrachain interaction J from the paramagnetic region of the experimental susceptibility. The magnetic susceptibility in the paramagnetic region is given by [8]:

$\chi = C / T - Cp$ where

$Cp = 2\ zJS(S+1)/3\ k_B \approx \theta$ (1)

J is the nearnest neighbor exchange interaction and z is the number of nearnest neighbors. The exchange integral, calculated using eq (1) from the experimental value $\theta$ is $zJ/k_B$ = 4.35 K.

We can get a rough estimate of the antiferromagnetic interchain interaction exchange constant from the peak value of $\chi_m$ by[9] :

$-2\ z_{AF}\ J_{AF}/k_B = Ng^2\mu_B{}^2S/2k_B\ \chi_{peak}$ (2)

Since the value of $\chi_{peak}$ = 0.1807 emu.mol$^{-1}$, g = 2.1 will be used as a fixed parameter which compares reasonably well with the various results quoted in the literature[10], we get -2.28 K for the interchain exchange constant.

The magnetic susceptibility vs. temperature of $Co_2P_4O_{12}$ compound is plotted in figure 3. A characteristic feature of the curve is a sharp maximum at T = 8 K which then decreases rapidly as the temperture is lowered. This indicates that a transition from the paramagnetic to an antiferromagnetic order phase takes place. We noted that paramagnetic Curie constant and paramagnetic temperature are 6.25 emu.K.mol$^{-1}$ and -3 K, respectively. The value of the magnetic moment deducted was 5$\mu_B$ per mol.

As in such compounds that contain cobalt atoms, are a good example where spin-orbit interaction contribute to the magnetic behaviour at high temperature. This can be seen in figure 3, from the positive curveture of $\chi_m$T vs. temperature at increasing temperature. At low temperature, the value of $\chi_m$T decreases with decreasing temperature, resulting from the manifestation of antiferromagnetic intrachain interaction.

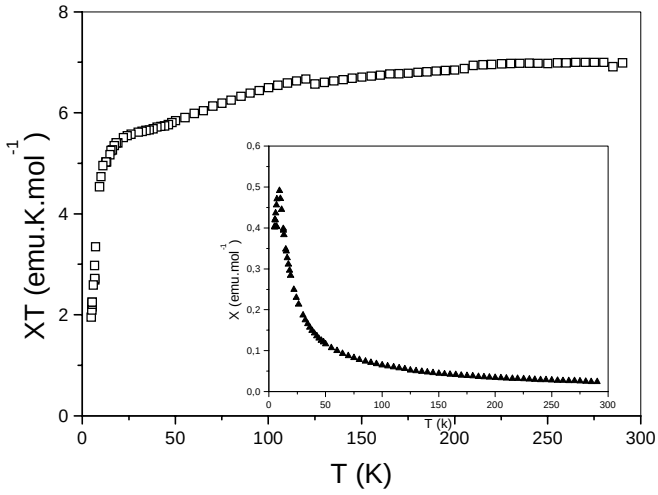


Figure 3 : Variation of the product $\chi$T and susceptibility (in insert) vs. temperature of $Co_2P_4O_{12}$.

Figure 4 shows plot of the magnetic susceptibility and the reciprocal magnetic susceptibility vs. temperature of $Cu_2P_4O_{12}$ compounds. From the fit of the susceptibility to Curie-Weiss law, the value C = 0.87 emu.K.mol$^{-1}$ and $\theta$ = -10.3 K are obtained. The negative value of $\theta$ indicates the existence of antiferromagnetic interaction. The susceptibility increases rapidly below 25 K. Obviously, such behaviour appears in some systems with alternating Landé factors[11].

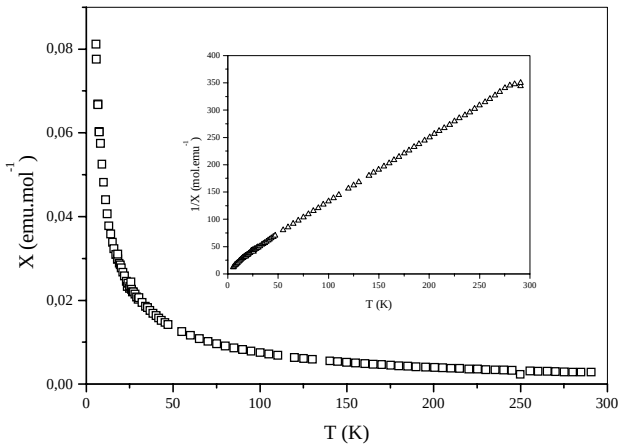


Figure4: Magnetic susceptibility and inverse of susceptibility vs. temperature of $Cu_2P_4O_{12}$.

In order to confirm the tridimensional transition in both $Co_2P_4O_{12}$ and $Ni_2P_4O_{12}$, we are expected to measure their specific heat between 2 and 30 K. The result is as shown in figure 5, the specific heat exhibit a sharp maximum at 14 K for $Ni_2P_4O_{12}$ and at 9 K for $Co_2P_4O_{12}$. This neatly confirms the transition at the same temperatures showed the maximum of susceptibilities respectively. Furthermore, the small anomaly found at T = 6 K in $Co_2P_4O_{12}$, probably originates from crystal field effect. We can also notice the important lattice specific heat contribution in both systems where temperature increases, according to $T^3$ law.

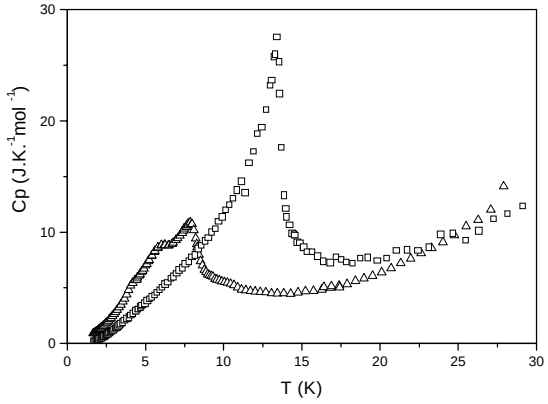


Figure 5: Variation of the specific heat with temperature of $Ni_2P_4O_{12}$ (square) and $Co_2P_4O_{12}$ (triangle).

The magnetic properties observed in our systems, corroborate the geometrical connexion between magnetic orbitals (orbital containing unpered electron) of metallic ions via the ligand (oxygen) orbital. In sens here a strong overlap leads to an antiferromagnetism, and orthogonal orbitals stabilizes a ferromagnetic couplage[12,13]. The developement of this study with theoretical approach is in progress.

## IV.Conclusion

We have attempted to determine some thermodynamic properties of important phosphate compounds that belong to isostructural $M_2P_4O_{12}$ class (M = Cu, Co, Ni). Their magnetic properties exhibit low dimensional system behaviours, varied from ferromagnetic ($Ni_2P_4O_{12}$) to antiferromagnetic ($Co_2P_4O_{12}$ and $Cu_2P_4O_{12}$) ordering. We have detected their 3d transition temperature.

**Acknowledgements**

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**References**

[1] M. Belaïche, J. Aride, T. Biaz, A. Moqine, A. Boukhari and M. Drillon. Phase transition, 13, 149 (1988)
[2] A. Moqine, A. Boukhari and S. Flandrois, Mat. Res. Bull., 22, 965 (1987)
[3] M. Belaïche, M. Bakhache, M. Drillon, A. Derrory and S. Velminot, Physica B, 305, 270 (2001)
[4] M. Laûgt, J. Cuitel, I. Tordjman and G. Bassi, Acta crystalogr. B28, 201 (1972)
[5] A. G. Nord, Acta Chem. Scand. A37, 539 (1983)
[6] A. G. Nord, Cryst. Struct. Commum. 11, 1467 (1982)
[7] A. G. Nord and K. Lindberg, Acta Chemica Scand. A 29, 1 (1975)
[8] C.P. Landee and R.D. Willett, J. Appl. Phys.52, 2240 (1981)
[9] J. S. Smart, Effective field Theories of Magnetism (Saunders, Philadelphia, 1986)
[10] M. Steiner, Solid State Commun. 11, 73 (1972) ; Ch. Rosinski and B. Elschner, J. Magn. Magn. Mater, 4, 193 (1977)
[11] E. Coronado, M. Drillon, P.R. Nugteren, L.J. de Jongh, and D. Beltron, J. Am. Chem. Soc., 110, 3907 (1988)
[12] J. B. Goudnough, Phys. Rev. 100, 564, (1955); Phys. and Chem. Solids 6, 287 (1958)
[13] J. Kanomari, Phys. and Chem. Solids 10, 87 (1959)