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Magnetic and thermodynamic properties and magneto-structural correlation of the diphosphate $ZnCoP_2O_7$

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ABSTRACT

The structure of the mixed diphosphate $ZnCoP_2O_7$ is characterized by the cationic order between the diamagnetic and paramagnetic ions. The Co^{2+} ions are lodged in octahedral sites whereas the Zn^{2+} ions occupy distorted square pyramids. The octahedrons CoO_6 share a common edge and form dimers Co_2O_{10} separated by dimers of zinc, which confers to this compound a low dimensionality character. Magnetic susceptibility shows that $ZnCoP_2O_7$ is antiferromagnetic. The correlation magneto-structural confirms the presence of Co^{2+} dimers. The magnetic specific heat of $ZnCoP_2O_7$ shows a large maximum characteristic of a low dimensionality system.

KEYWORDS

Diphosphate; zinc cobalt; structure; magnetism; E.P.R

Introduction

The diphosphates of transition elements 3d studied until now, rarely showed a restricted order. In the case of the simple diphosphates $M_2P_2O_7$ (M = Cr, Mn, Fe, Co, Ni, Cu), the M^{2+} ions are distributed in plans, which confers to these compounds a two-dimensional character [1–15]. The mixed diphosphates $MM'P_2O_7$ (M, M' = Mn, Fe, Co, Ni) Also present a distribution of the M^{2+} and M'^{2+} ions in plans. So, the two-dimensional character is kept [16–23]. Among our works, we obtained a one-dimensional character in $LiNi_{1.5}P_2O_7$ by substituting all Ni^{2+} ions of coordinence 5 in α-$Ni_2P_2O_7$ by Li^+, which allowed the formation of zigzag chains constituted by NiO_6 octahedrons [22]. In reference to our works when we tried to reduce the dimensionality in the mixed diphosphates $Zn_xM_{2-x}P_2O_7$ ($0 \leq x \leq 2$) (M = Mn, Co, Ni, Cu) by Zn^{2+} and in $LiNi_{1.5}P_2O_7$ by Li^+ [21], [23], we prepared in the form of single crystals, the mixed diphosphate $ZnCoP_2O_7$. Its crystalline structure is characterized by the presence of quasi-isolated Co^{2+}dimers, separated by Zn^{2+} dimers, which confers to this compound a low dimensionality behavior [26].

Measures of magnetic susceptibility, magnetic specific heat and electron paramagnetic resonance were realized on the diphosphate $ZnCoP_2O_7$ to correlate these properties to its crystalline structure.

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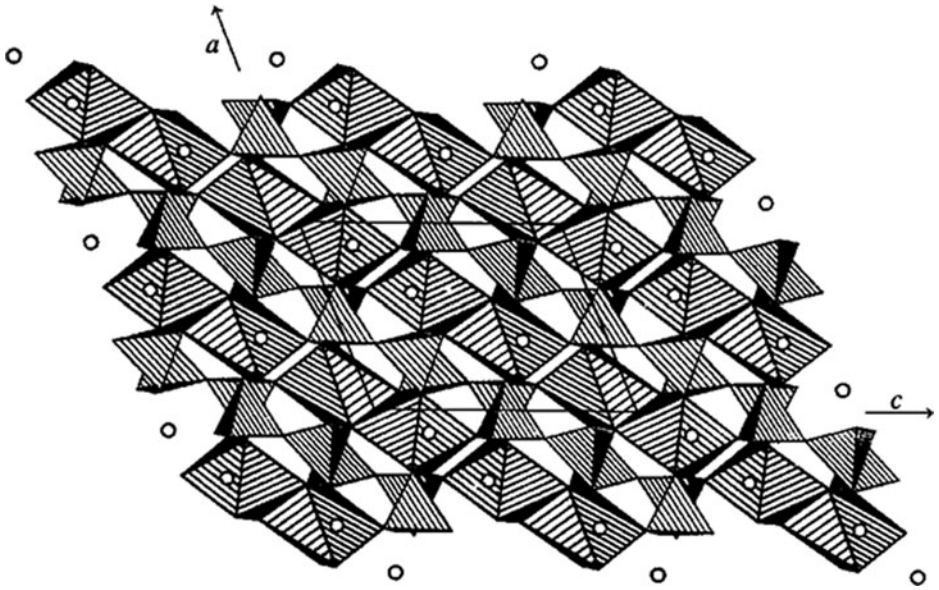

Figure 1. Projection of the $ZnCoP_2O_7$ structure in the plan (010) Zn^{2+} ions are represented by circles and Co^{2+} by octahedrons.

I. Structure description

The diphosphate $ZnCoP_2O_7$ crystallize in the monoclinic system with the space group $P2_1/n$. Its structure is built from sheets of $P_2O_7^{4-}$ groups parallel to the crystallographic plan (101), linked by layers of zinc and cobalt dimmers (figure 1). The $P_2O_7^{4-}$ groups have a staggered conformation which is generally observed in diphosphates of 3d transition elements. Consequently, this compound belongs to the structural type thortveitite. The Co^{2+} cations are lodged in octahedrons. Two octahedrons share between them an edge and share summits with the nearby $P_2O_7^{4-}$ groups and so, tunnels directed along the direction [100] are formed. The pairs of Zn^{2+} ions are located in these tunnels (figure 2). The Zn^{2+} ions have five nearby close oxygens.

The average distance Zn-O is 2.048 Å. The Co^{2+} ions occupy octahedral sites slightly deformed. The average distance Co-O is 2.11 Å. The intra-dimer distance Co …Co is 3.27 Å, but the shortest inter-dimer distance is 5.01 Å. This result reveals that dimers of cobalt are almost isolated and justify the classification of this diphosphate in a low dimensionality system (0D).

II. E. P. R

The EPR spectrum of $ZnCoP_2O_7$ diphosphate (figure 3) obtained at ambient temperature shows the existence of two components of g: $g_{//} = 4.54$ et $g_{\perp} = 2.11$. These values are generally observed for the Co^{2+} ions in a crystalline field with axial symmetry [27]. Indeed, in $ZnCoP_2O_7$ isostructural to α-$Co_2P_2O_7$, the Co^{2+} ions occupy pentahedral and distorted octahedral sites. The effect of axial symmetry of the crystalline field due to the distortions of sites in addition to the spin - orbit coupling within Co^{2+} ions leads to these anisotropic values of g.

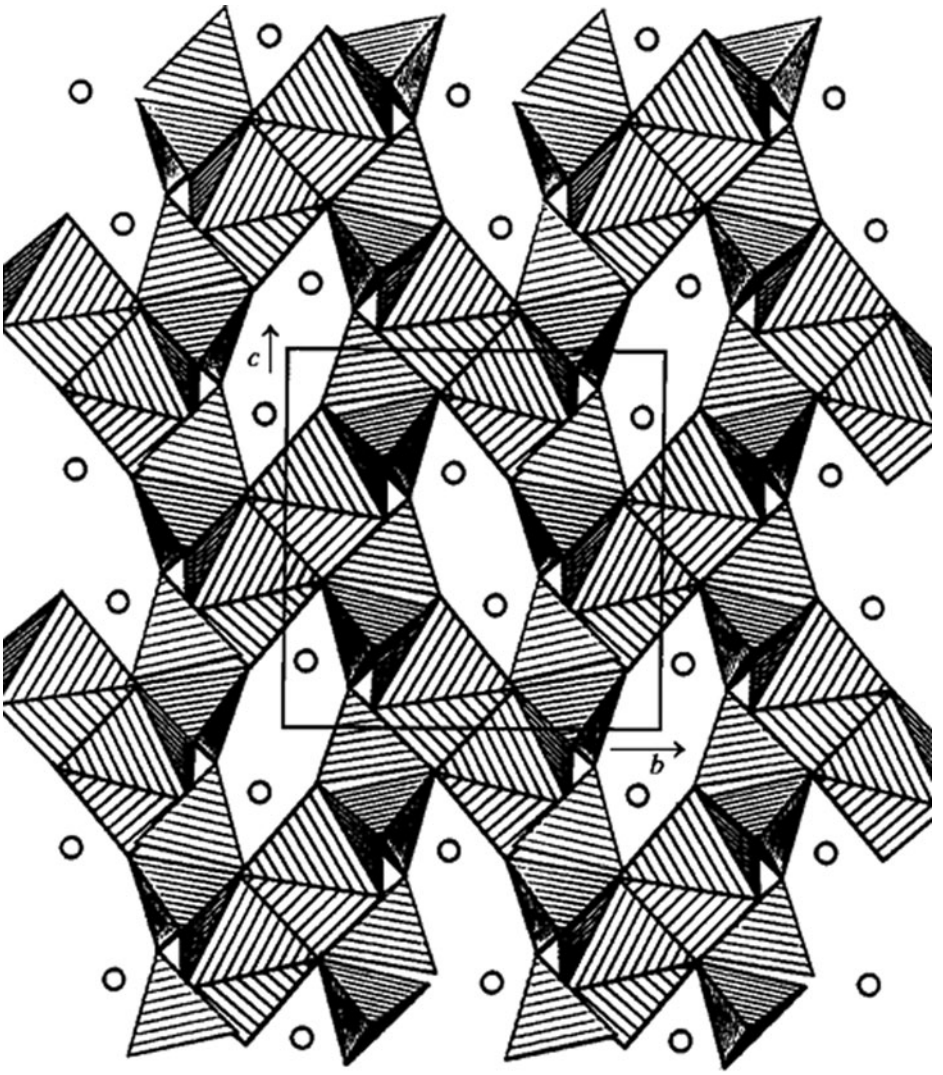

Figure 2. Projection of the $ZnCoP_2O_7$ structure in the plan (100) Zn^{2+} ions are represented by circles and Co^{2+} by octahedrons.

III. Magnetic susceptibility

The curve of thermal variation of the inverse magnetic susceptibility (figure 4a) presents a Curie-Weiss behavior at high temperatures. The fast decrease of the product χ.T at low temperatures is due to the compensations between magnetic moments (figure 4b). At high temperatures, the curve of thermal variation of the product χ.T shows two plates corresponding to two values of C (Curie constant) on both sides of $T = 50$ K. Indeed, in octahedral field, the fundamental state of Co^{2+} ions is $^4T_{1g}$, under the action of an axial distortion of the crystal field in combination with the spin-orbit coupling, this state is separated into six pairs of Kramer. Thus, the ground state is a doublet. At high temperatures ($T > 50$K), under the action of thermal agitation, electrons occupy higher energy levels. The number of total spin is $S = 3/2$. At low temperatures ($T \leq 50$ K), only the fundamental levels are populated with an effective spin $S = 1/2$; this causes a decrease of the Curie constant, and therefore the product χ.T decreases. This behavior is reflected on $\chi^{-1}(T)$ curve by a change in slope at 50 K.

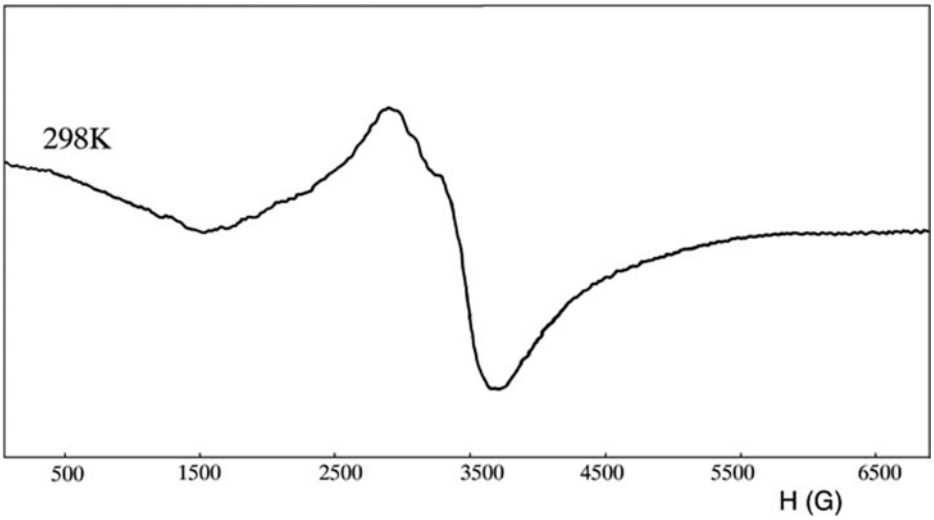

Figure 3. EPR Spectrum of $ZnCoP_2O_7$ diphosphate.

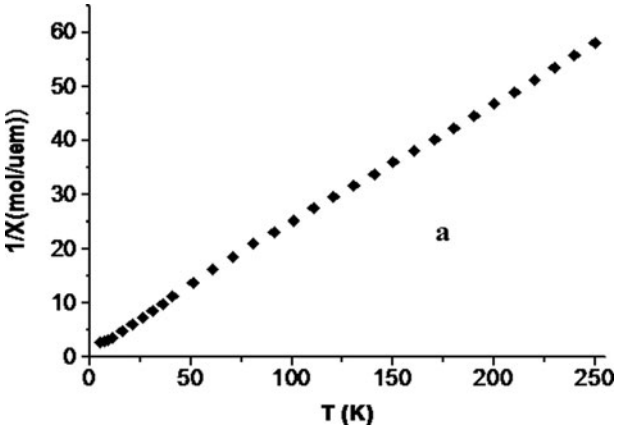

Figure 4a. Thermal variation of the inverse magnetic susceptibility.

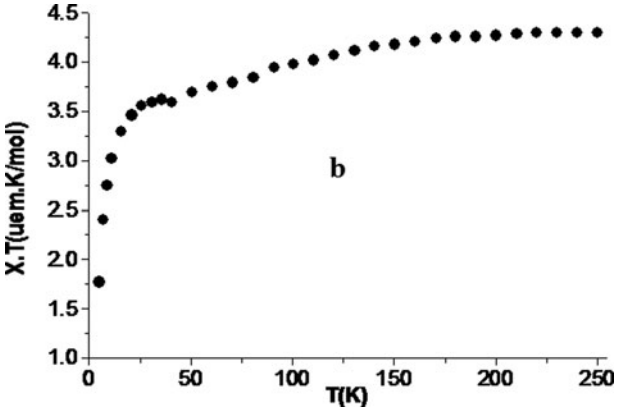

Figure 4b. Thermal variation of the product χ.T of the diphosphate $ZnCoP_2O_7$.

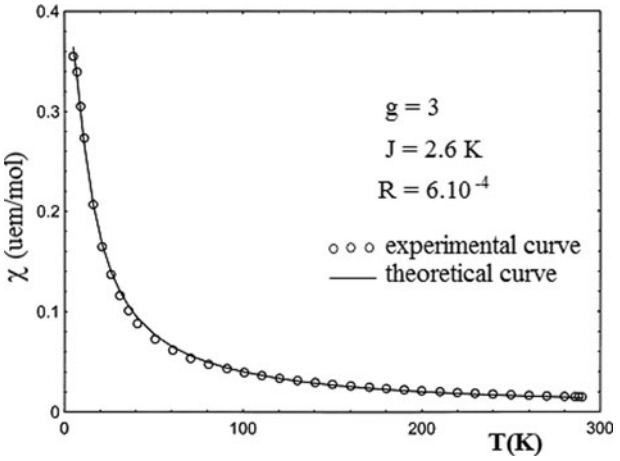

Figure 5. χ(T) thermal variation of $ZnCoP_2O_7$: (o) experimental curve, (-) theoretical curve.

The high experimental value of C (*3.3* uem.K / mol) can be justified by the strong spin-orbit coupling in the Co^{2+} ions. The negative value of Θp (*−6* K) shows that the dominant interactions are antiferromagnetic.

IV. Magneto-structural corrélation

The structure of $ZnCoP_2O_7$ reveals that the Co^{2+} ions are distributed in an orderly way in dimers of two octahedrons Co_2O_6 linked by one edge and separated from each other by zinc dimers. The intradimer distance Co …Co is 3.27 Å and the shortest interdimer distance is 5.01 Å. These results show that the dimers of Co^{2+} are substantially isolated; which classifies this compound in a low-dimensional system (0D). To corroborate this result, crystals of this compound were selected and grounded. The powder obtained is used for the measurement of magnetic susceptibility.

The application of Van Vleck equation for a dimer of spin 3/2 allowed to have the form of magnetic susceptibility:

$$\chi(T) = \frac{2N(g\mu B)^2}{KT} \frac{\exp(2J/kT) + 5\exp(6J/kT) + 14\exp(12J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT)}$$

The fit of the experimental data by this formula led to the following parameters:

- Lande factor g = *3*
- Exchange Integral J = *−2.6* K.

The high value of g is close to the average of $g_{//}$ and $g_{\perp}$ obtained by EPR and confirms the anisotropy of the octahedral sites occupied by the Co^{2+} ions.

The value of negative and low J shows that the interactions are weak antiferromagnetic. This is explained by the absence of magnetic order above *4* K. The temperature dependence curve of experimental χ(T) coincides with the theoretical curve (Figure 5). this justifies the dimer model.

V. Magnetic specific heat

The measurement of the specific heat is performed on the powder of $ZnCoP_2O_7$ crystals grounded (figure 6). From the temperature *17* K, Cp increases rapidly under the influence

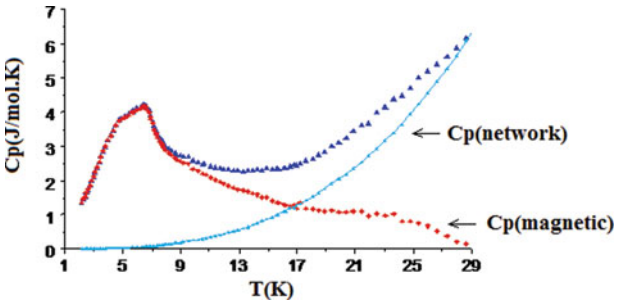

Figure 6. Thermal variation of the magnetic specific heat of $ZnCoP_2O_7$.

of the network contribution following the law: Cp(network) = aT^3 ($a = 3.10^{-4}$). The deduction of Cp(network) allows deducing the magnetic specific heat Cp (magnetic).

Cp has a wide maximum around *6.2* K characteristic of a low-dimensional order. This result seems very logical knowing that the structure of $ZnCoP_2O_7$ is formed by almost isolated cobalt dimers separated by dimers of zinc and by $P_2O_7^{4-}$ groups. We remind that Cp of α-$Co_2P_2O_7$ has a sharp maximum of λ type characteristic of a three dimensional order [21].

VI. Conclusion

We conclude that the diphosphate $ZnCoP_2O_7$ has an original crystal structure justified by the cationic order between diamagnetic ions and paramagnetic ions. The order has never been observed before in diphosphates of 3d transition elements where the ions are usually distributed in planes and form hexagonal honeycomb. The presence of isolated dimers of paramagnetic ions Co^{2+} gives to this compound a low-dimensional character EPR measurements confirmed the form of the sites occupied by Co^{2+} ions and the nature of their deformation. Measurements of the magnetic susceptibility show that the diphosphate $ZnCoP_2O_7$ is antiferromagnetic. The correlation between the structure and magnetic properties confirms its ranking in a low-dimensional system. The magnetic specific heat of this compound presents a rather wide maximum characteristic of low-dimensional system; this result is in good agreement with the structural sequence of Co^{2+}dimers.

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