

# Magnetic Properties of the $\text{Fe}(\text{PO}_3)_3$ Metaphosphate

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Received November 4, 1998; in revised form February 19, 1999; accepted March 9, 1999

The  $\text{Fe}(\text{PO}_3)_3$  compound has been synthesized by solid state reaction. The crystal structure consists of a three-dimensional network, with infinite  $[\text{PO}_3]_\infty$  chains of  $|\text{PO}_4|$  tetrahedra and isolated  $|\text{FeO}_6|$  octahedra, where the Fe(III) ions occupy three different crystallographic positions. The IR spectrum of the compound shows bands characteristics of metaphosphate groups with chain structure. The X-band EPR spectra on polycrystalline samples are isotropic with a  $g$  value of approximately 2.0, which remains unchanged with variation in temperature. The intensity of the signals increases with decreasing temperature reaching a maximum at about 12 K and at lower temperatures the intensity decreases, becoming silent at 4.2 K. Magnetic measurements at high magnetic fields show a three-dimensional antiferromagnetic behavior, with a  $J/k$  value of  $-0.36$  K. However, the magnetic study at less magnetic fields reveals the existence of a weak ferromagnetism intrinsic to the sample. © 1999 Academic Press

## INTRODUCTION

The solid state chemistry of polyphosphates in which the transition metal exhibits a trivalent oxidation state is traditionally considered unusual (1). The great ability of the phosphate frameworks to stabilize these oxidation states is produced for the relatively high charge in  $(\text{PO}_4)^{3-}$  tetrahedra that favors the formation of anionic frameworks with a high degree of mechanical, chemical, and thermal stability (2,3). These compounds exhibit interesting properties such as magnetic, heterogeneous catalysis, ionic exchange, and optical, with potential applications (2,3).

The  $\text{Fe}(\text{PO}_3)_3$  metaphosphate belongs to a series of polyphosphates with the general formula  $M(\text{PO}_3)_3$  ( $M = \text{Al}, \text{Cr}, \text{Ga}, \text{V}, \text{Mn}, \text{Fe}, \text{Rh}, \text{Ti}, \text{Mo}, \text{Sc}, \text{In}, \text{and Ti}$ ) (4). These compounds are polymorphic and can adopt up to five crystalline forms, which are denoted A, B, C, D, and E (4). Most of the well-investigated compounds in this class of polyphosphates belong to the C form, including the  $\text{Fe}(\text{PO}_3)_3$  compound. The crystal structure of this C form

can be described as formed by isolated  $\text{MO}_6$  octahedra linked through infinite  $[\text{PO}_3]_\infty$  chains of  $\text{PO}_4$  tetrahedra (Fig. 1). Each  $\text{MO}_6$  group is bridged to six neighboring  $\text{MO}_6$  octahedra by phosphate groups and each octahedron shares its six apexes with six different  $\text{PO}_4$  tetrahedra. These groups are also placed in adjacent layers and lead to a three-dimensional network, in which the metallic cations occupy three different crystallographic positions (5–7).

In past years, and as a part of our research in the field of the phosphate and arsenate compounds, we have synthesized and studied different polyphosphates with trivalent transition metal ions of formula  $M(\text{PO}_3)_3$  ( $M = \text{Ti}, \text{V}, \text{Cr}, \text{and Mo}$ ) (8–10). Taking into account the structural features of these compounds and the nature of the metallic cations, their magnetic properties are expected to be very interesting. In this way, the magnetic study on these compounds reveals different types of magnetic exchange interactions, which range from antiferromagnetic to ferromagnetic for the chromium or molybdenum phases and the titanium compound, respectively. In the vanadium metaphosphate, the magnetic behavior is determined by both the antiferromagnetic interactions and the zero-field splitting parameter characteristic of this cation. Furthermore, the existence in such metaphosphates of many possible exchange pathways makes it difficult to determine the dominant interactions. The present work reports on the magnetic behavior of the  $\text{Fe}(\text{PO}_3)_3$  phase, which presents a phenomenon of weak ferromagnetism. A comparative study with the related chromium and molybdenum compounds is also carried out.

## EXPERIMENTAL

### *Synthesis of the Compound*

$\text{Fe}(\text{PO}_3)_3$  was synthesized starting with a mixture of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $(\text{NH}_4)\text{H}_2\text{PO}_4$ , with a molar ratio Fe:P of 1:10. The mixture was placed in an alumina crucible, heated at 300°C for 4h, and then heated up to 800°C followed by a rapid cooling to room temperature. Light green polycrystalline samples were obtained. The compound was washed with water and dried over  $\text{P}_2\text{O}_5$  for 24 h.

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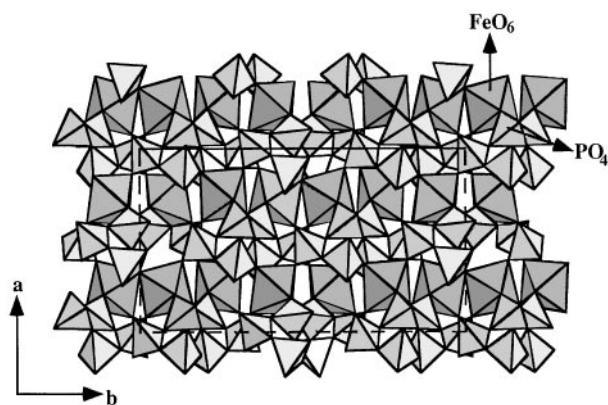


FIG. 1. Crystal structure of  $\text{Fe}(\text{PO}_3)_3$ .

The metal ion and phosphorus contents were confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (Found: Fe, 19.0; P, 31.4,  $\text{Fe}(\text{PO}_3)_3$  requires: Fe, 19.1; P, 31.7).

#### X-Ray Crystallography

A PHILIPS X'PERT automatic powder diffraction system, operating at 40 kV, 40 mA, with  $\text{CuK}\alpha$  radiation, was used to record the X-ray powder diffraction pattern of the compound. A  $\omega$ - $2\theta$  scan was performed, with steps of  $0.02^\circ$  in  $2\theta$  and a fixed counting time of 6 s. The X-ray powder diffraction pattern was indexed by using the TREOR-4 program (11) in a monoclinic unit cell with the space group  $Ic$ . The refined unit-cell parameters are  $a = 9.56(1)$ ,  $b = 19.46(4)$ ,  $c = 10.542(7)$  Å, and  $\beta = 102.5(1)^\circ$ . These values are similar to those observed for other  $M(\text{PO}_3)_3$  ( $M = \text{Al, Ti, V, Cr, and Mo}$ ) polyphosphates belonging to the C form, whose structures were resolved from X-ray single crystal data (5, 6, 12–14), and indicate the isostructural character of these metaphosphates.

#### Physical Measurements

IR spectrum (KBr pellet) was obtained with a Nicolet FT-IR 740 spectrophotometer. A Bruker ESP 300 spectrometer, operating at X band, was used to record the EPR polycrystalline spectra between 4.2 and 300 K. The temperature was stabilized by an Oxford Instrument (ITC 4) regulator. The magnetic field was measured with a Bruker BNM 200 gaussmeter and the frequency inside the cavity was determined using a Hewlett-Packard 5352B microwave frequency counter. Magnetic measurements were performed on polycrystalline samples between 1.8 and 300 K, using a Quantum Design SQUID magnetometer (MPMS-7).

## RESULTS AND DISCUSSION

### IR Spectroscopy

The most important bands observed in the IR spectrum of the  $\text{Fe}(\text{PO}_3)_3$  compound are shown in Table 1, together with those for other isostructural metaphosphates, belonging to the C form, for comparison. The compounds exhibit a strong band above  $1220\text{ cm}^{-1}$  that is assigned to the  $\nu_{\text{as}}$  ( $\text{P-O}_{\text{ext}}$ ) stretching antisymmetric vibration of the metaphosphate groups. Additional bands in the  $1010$ – $1160\text{ cm}^{-1}$  region can also be observed due to the simultaneous existence of  $\text{PO}_2$  and  $\text{PO}_3$  groups in the phosphate anions. The band observed at approximately  $970\text{ cm}^{-1}$  in the compounds is attributed to the antisymmetric stretch  $\nu_{\text{as}}$  ( $\text{P-O}_{\text{int}}$ ) of the P–O–P bridge bonds. Likewise, there are at least three or four signals of medium intensity in the range  $675$ – $775\text{ cm}^{-1}$ , corresponding to the symmetric stretch  $\nu_{\text{s}}$  ( $\text{P-O}_{\text{int}}$ ) of P–O–P bridge bonds, which is characteristic of metaphosphates with chain structure. Finally, the IR spectra of the compounds exhibit bands with poor resolution in the range  $470$ – $615\text{ cm}^{-1}$ . These bands can be as-

TABLE 1  
Selected IR Bands ( $\text{cm}^{-1}$ ) and Empirical Assignments for Several  $M(\text{PO}_3)_3$  ( $M = \text{Ti, V, Cr, Mo, Fe}$ ) Metaphosphates between  $400$  and  $1500\text{ cm}^{-1}$

Assignment	Ti <sup>a</sup>	V <sup>a</sup>	Cr <sup>a</sup>	Mo <sup>a</sup>	Fe
$\nu_{\text{as}}(\text{P-O}_{\text{ext}}) \text{PO}_2 $	1385 vs	1240 vs	1240 vs	1250 vs	1230 vs
	1115 s	1150 s	1160 s		
			1130 s	1125 s	1120 s
$\nu_{\text{s}}(\text{P-O}_{\text{ext}}) \text{PO}_2 $	1090 s	1095 s	1095 vs	1085 s	1075 s
$\nu(\text{P-O}_{\text{ext}}) \text{PO}_3 $	1040 s		1050 s		
		1020 s	1020 s	1025 s	1020 s
				1010 s	
$\nu_{\text{as}}(\text{P-O}_{\text{int}}) \text{P-O-P} $	960 s	975 s	975 s	955 s	970 s
	770 m	770 m	775 m	775 m	
	750 m	765 m	760 w		750 m
$\nu_{\text{s}}(\text{P-O}_{\text{int}}) \text{P-O-P} $	715 m	715 m		745 m	
			725 m		
				705 m	705 m
	690 w	685 m	685 w	675 m	675 m
$\nu_{\text{as}}(\text{M-O})$				610 w	615 w
	560 m	560 m	570 m		580 w
$\delta_{\text{as}}(\text{O-P-O})$			560 m	545 m	545 m
		510 m	520 m		
			490 m	500 s	505 m
	470 m	480 m		470 m	470 m

Note. vs, very strong; s, strong; m, medium; w, weak.  
<sup>a</sup>Taken from Refs. (8) and (10).

signed to the antisymmetric stretching modes in the  $\text{MO}_6$  octahedra, probably coupled with the antisymmetric bending modes of the chain groups  $[\delta_{\text{as}}(\text{O-P-O})]$  (15–17).

### EPR Spectroscopy

The powder X-band EPR spectra of  $\text{Fe}(\text{PO}_3)_3$  at different selected temperatures are shown in Fig. 2a. In all cases isotropic signals centered around  $g = 2$  were observed. These signals are characteristic of Fe(III) cations in octahedral environments without large tetragonal distortion. The room temperature spectrum ( $g = 1.99$ ) fits exactly the characteristics of a Lorentzian curve being the same result obtained for all spectra registered down to 10 K. Below 10 K the fits are not considerably good. The temperature dependence of the intensity and linewidth of the signal calculated by simulations of the experimental spectra to Lorentzian curves is displayed in Fig. 2b. The  $g$  value remains apparently unchanged in all of the temperature ranges studied. The intensity of the signal increases with decreasing temperature, reaches a maximum at about 12 K,

and after that rapidly decreases. In fact, at 4.2 K no relevant signal could be observed. As can be deduced from the straight line that fits the  $1/I$  vs  $T$  curve, at high temperature the susceptibility of the compound follows a Curie–Weiss law and no short order effects are detectable above 30 K.

As long as the high temperature condition ( $kT \gg H_z, H_{\text{ex}}, H_{\text{dip}} \dots$ ) is expected to be satisfied, the linewidth is observed to have low temperature dependence. Only a small increase is observed between RT and 50 K probably due to the dipolar homogeneous broadening. Furthermore, when the temperature is decreased the linewidth increases rapidly reaching a maximum at 8 K. This behavior is characteristic of systems with a three-dimensional order and, in this case, it must be of antiferromagnetic nature considering the thermal evolution of the intensity of the signal (18, 19). The apparent temperature independence of the resonance field is also in good agreement with a three-dimensional behavior with quasi-isotropic interactions. In any case, the presence of three different Fe(III) sites and the relatively large linewidths (430–1050 G) imply that the conclusions obtained from the powder spectra must be considered with caution. In fact, the observed isotropic signal is the result of the collapse by exchange of those expected for the three different Fe(III) ions.

### Magnetic Properties

The temperature and field dependencies of the magnetic susceptibility and the magnetization have been investigated. At first glance, the thermal behavior of the magnetic susceptibility seems to be that expected for a three-dimensional system with an antiferromagnetic ordering at about 8 K. When the magnetic measurements were carried out under a magnetic field of 1 T one can observe a maximum in the  $\chi_m$  vs  $T$  curve centered at about 8 K (Fig. 3) and a continuous decrease in the magnetic effective moment with decreasing temperature from room temperature to 4.2 K. However, more detailed experiments have shown that the magnetic susceptibility is strongly dependent on the magnetic field at temperatures less than 10 K (Fig. 3). Moreover, the magnetic history of the sample also has an important influence on the observed results. These facts suggest the presence of some ferromagnetic contributions in this compound.

The magnetization vs field curves registered above (10 K) and below (5 K) the ordering temperature are apparently not too much different but two important points must be noticed. In both cases the magnetization curves are nearly linear up to 7 T, but at lower temperatures a small change on the slope is observed at about 0.04 T (inset in Fig. 3). Moreover, a weak magnetization (about  $50 \text{ cm}^3 \text{Oe/mol}$ ) is retained at zero field. Taking into account these results, we performed magnetization measurements vs temperature at a field of 100 Oe. The curves obtained are displayed in Fig. 4. The field-cooled magnetization (FC) shows a rapid

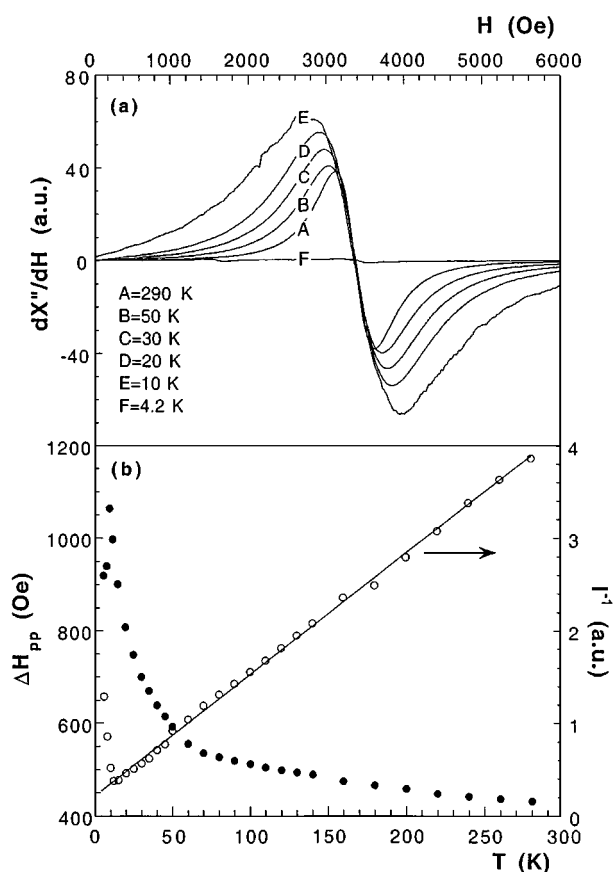


FIG. 2. (a) Powder X-band EPR spectra at different temperatures and (b) temperature dependence of  $1/I$  of the signal and the linewidth curves for the  $\text{Fe}(\text{PO}_3)_3$  compound.

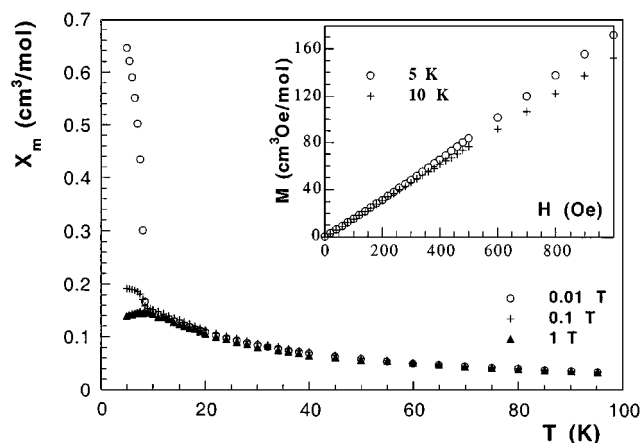


FIG. 3. Thermal dependence of  $\chi_m$  at different magnetic fields for  $\text{Fe}(\text{PO}_3)_3$ . Inset shows the magnetization vs field curves, below and above the Néel temperature.

increase in  $M$  below  $T_N = 8$  K. The zero-field-cooled magnetization (ZFC) measured upon cooling to 4.2 K in zero field and heating the sample under 100 Oe is less than that of the FC below  $T_N$  (it remains practically constant) and completely similar above the critical temperature. Finally, when the sample is cooled within the field and upon further heating in zero field, one can observe (inset in Fig. 4) that the remanent magnetization decreases with increasing temperature and vanishes above 8 K. All these features are characteristic of a magnetically ordered state below 8 K (20), with the presence of a weak ferromagnetism intrinsic to the sample.

As mentioned before the data above 10 K are not affected by the magnitude of the external field. Thus, measurements at higher fields (0.1 T) were carried out to study the whole behavior of the magnetic susceptibility without any appreci-

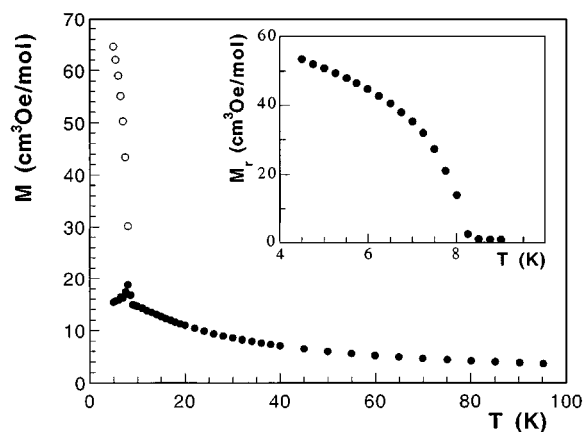


FIG. 4. Thermal dependence of the magnetization at ZFC (black circles) and FC (open circles) for the  $\text{Fe}(\text{PO}_3)_3$  compound. Inset shows the zero-field magnetization curve vs  $T$  for the  $\text{Fe}(\text{PO}_3)_3$  compound cooled under a magnetic field of 100 Oe.

able sensitivity losses in the measurements. From a plot of the reciprocal molar magnetic susceptibility vs. temperature classical Curie–Weiss behavior can be deduced above 20 K (see Fig. 5), being  $C_m = 4.40 \text{ cm}^3\text{K/mol}$  and  $\theta = -13.3$  K. From the calculated Curie constant a  $g$  value of 2.00 can be derived, in good agreement with that calculated from the EPR spectra and with the topology of the Fe(III) octahedra in the title compound. The negative Weiss temperature and the observed decrease in the  $\chi_m T$  product with decreasing temperature (Fig. 5) are indicative of the existence of antiferromagnetic exchanges as major interactions in this compound.

Considering the structural features of the  $\text{Fe}(\text{PO}_3)_3$  compound superexchange interactions via  $|\text{PO}_4|$  tetrahedra can only be expected. Despite the complexity of the three-dimensional arrangement a simple cubic network can be considered to be an acceptable description of the stacking of the Fe(III) ions and can be utilized to obtain an approximate value of the exchange parameter. Considering the usual isotropic magnetic behavior of the Fe(III) ions, a Heisenberg hamiltonian can be proposed as a theoretical approach to the magnetic behavior,

$$H = -2J \sum_{(i<j)} S_i S_j.$$

Using the high temperature series expansion developed by Rushbrooke and Wood (21) the following analytical expression for the magnetic susceptibility is deduced for a Heisenberg simple cubic antiferromagnetic system with  $S = 5/2$ ,

$$\chi_m = \frac{35 Ng^2 \beta^2}{12kT} \left[ 1 + \frac{35}{x} + \frac{221.67}{x^2} + \frac{608.22}{x^3} + \frac{26049.6}{x^4} + \frac{210986.5}{x^5} + \frac{8014980}{x^6} \right]^{-1},$$

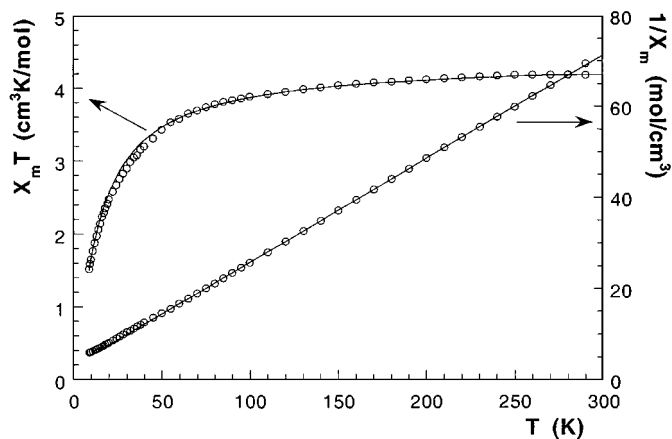


FIG. 5. Thermal dependence of the  $\chi_m T$  product and  $1/\chi_m$  for  $\text{Fe}(\text{PO}_3)_3$ .

where  $x = kT/J$ ,  $N$  is Avogadro's number,  $\beta =$  Bohr magneton, and  $k =$  Boltzmann constant.

The best fit of the experimental data to the above equation was obtained for  $g = 2.00$  and  $J/k = -0.36$  K, and it is represented by the solid line in Fig. 5. Despite the differences between the real system and the employed model, the calculated curve follows the experimental data rather well. Moreover, for such a system a sharp maximum in the thermal evolution of the magnetic susceptibility is expected at 8.5 K, in good agreement with the experimental data. Therefore, it can be concluded that the magnetic behavior of the iron metaphosphate is well described as a three-dimensional Heisenberg antiferromagnetic with a  $J/k$  value about 0.4 K.

In the related chromium and molybdenum metaphosphates similar behaviors were observed, with  $J/k$  values of the same magnitude:  $-0.30$  and  $-0.38$  K for Cr(III) and Mo(III) compounds, respectively, (8). However, for those metaphosphates field dependence phenomena were not detected at low temperatures. The above-described weak ferromagnetism observed in the iron metaphosphate is antiferromagnetic in origin, which must be provided from a not exactly antiparallel alignment of spins within an antiferromagnetic system resulting in a net magnetic moment in the ordered state (*canting* phenomenon). The presence of three different sites for the metallic ions in the structure with small differences in their magnetic anisotropy is probably the origin of the observed behavior, but this is not the unique cause because the same situation can be described for the Cr and Mo compounds. Furthermore, as occurring with the Cr(III) and Mo(III) ions, Fe(III) is usually characterized by its magnetically isotropic behavior (22). Therefore, the higher spin number in Fe(III) with respect to Cr(III) and Mo(III), which can give rise to new competing interactions, should be responsible for the observed weak ferromagnetism in the iron(III) metaphosphate.

#### CONCLUDING REMARKS

The synthesis of the  $\text{Fe}(\text{PO}_3)_3$  metaphosphate by solid state reaction and its magnetic properties are reported. The X-ray powder data and IR spectrum reveal its isostructural character with the metaphosphates of general formula  $M(\text{PO}_3)_3$  ( $M = \text{Al}, \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mo}, \dots$ ). The powder X-band EPR spectra at different temperatures show Lorentzian signals centered around  $g = 2$ , in good agreement with the presence of Fe(III) ions octahedrally coordinated without large tetragonal distortion. The thermal dependence of the linewidth and the intensity of the signals is characteristic

of a system with a three-dimensional ordering, antiferromagnetic in sign. The field-cooled magnetization curve shows an increase in the magnetization below Neél temperature. This fact is characteristic of the existence of a weak ferromagnetism intrinsic to the sample. A  $J/k$  value of  $-0.36$  K was obtained by fitting the experimental magnetic data to a simple Heisenberg cubic antiferromagnetic model. Similar weak antiferromagnetic behaviors were observed in the isostructural chromium and molybdenum metaphosphates. However, the last phases do not exhibit a *canting* phenomenon.

#### ACKNOWLEDGMENTS

This work was financially supported by the Ministerio de Educación y Ciencia and Universidad del País Vasco/EHU (Grants PB97-0640 and 169.310-EB149/98, respectively), which we gratefully acknowledge.

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