Crystal Structure Refinement and Magnetic Properties of Fe₄(P₂O₇)₃ Studied by Neutron Diffraction and Mössbauer Techniques

L. K. Elbouaanani,* B. Malaman,* R. Gérardin,*,1 and M. Ijjaali†

*Laboratoire de Chimie du Solide Minéral, Université Henri Poincaré-Nancy I, associé au CNRS (UMR 7555), B.P. 239, 54506 Vandoeuvre-les-Nancy Cedex, France; and † Laboratoire de Chimie Minérale, Faculté des Sciences et Techniques Fes Saiss, B.P. 2202,Fes, Morocco

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Fe₄(P₂O₇)₃ was prepared from Fe(PO₃)₃ and FePO₄ at 940°C under oxygen. The unit cell is monoclinic, space group $P2_1|n$, with a = 7.389(2) Å, b = 21.337(1) Å, c = 9.517(2) Å, $\beta = 90(1)^{\circ}$, and Z = 4. The crystallographic structure has been determined from a single crystal through direct methods and difference Fourier synthesis and refined to R = 0.10 ($R_w = 0.09$). The threedimensional framework is built up from Fe₂O₉ clusters of two face-sharing octahedra, linked by bent diphosphates P2O7 (P–O–P ~156°). Fe₄(P₂O₇)₃ is antiferromagnetic below $T_{\rm N} = 50$ K. The magnetic structure has been determinated by means of powder neutron diffraction. There are four antiferromagnetic iron sublattices corresponding to the four crystallographically distinct iron atoms. The magnetic moments are antiferromagnetically coupled inside the Fe₂O₉ dimers, in agreement with the Goodenough rules. They are parallel to the c axis and have 4.55(5) $\mu_{\rm B}$ value at 1.7 K. The magnetic interactions are discussed. Mössbauer spectra are fitted with four doublets and sextuplets in the paramagnetic and antiferromagnetic states, respectively. Their rather high isomer shifts are explained by the inductive effect. © 2002 Elsevier Science (USA)

Key Words: iron phosphate; single crystal; crystal structure; magnetic structure; ⁵⁷Fe Mössbauer spectrometry.

INTRODUCTION

Iron phosphates have been widely studied in our laboratory on account of their passivating properties and their importance in catalysis. Modaressi (1) and Ijjaali (2) have showed that $Fe_4(P_2O_7)_3$ is the ferric term of a four-diphosphate series, $Fe_2(P_2O_7)_3$, $Fe_7(P_2O_7)_4$, $Fe_3(P_2O_7)_2$, and Fe_4 $(P_2O_7)_3$, within which the first three terms have closely related structures.

In the iron(II) diphosphate $Fe_2(P_2O_7)$ the P_2O_7 groups connect FeO_6 octahedra which share edges to form thus a planar hexagonal lattice of octahedra. These sheets are parallely stacked. In the mixed-valent diphosphate $Fe_3(P_2O_7)_2$ the P_2O_7 groups connect Fe_3O_{12} trimers.

¹To whom correspondence should be addressed. E-mail: Rene. Gerardin@lcsm.uhp-nancy.fr.

These Fe₃O₁₂ units are constituted of a trigonal prism centered on Fe²⁺ which shares its two triangular faces with two FeO₆ octahedra occupied by Fe³⁺. In order to describe the Fe₇(P₂O₇)₄ structure from that of Fe₂(P₂O₇), B. Malaman *et al.* (4) suggest a mechanism based on the creation of vacancies on the iron lattice (namely a substitution $Fe^{2^+} \rightarrow Fe^{3^+}$). This mechanism leads to the series:

$$Fe_8(P_2O_7)_4(8Fe^{2+}) \to Fe_7\Box_1(P_2O_7)_4(5Fe^{2+}, 2Fe^{3+})$$

→ $Fe_6\Box_2(P_2O_7)_4(2Fe^{2+}, 4Fe^{3+}).$

Moreover, the magnetic properties of these three compounds have been determined (4) yielding a better knowledge of the exchange interactions in such compounds.

According to these results, it appeared very interesting to fully characterize the iron(III) term of the series: $Fe_4 (P_2O_7)_3 (Fe_{5.333}(P_2O_7)_4)$.

The iron(III) diphosphate $Fe_4(P_2O_7)_3$ was discovered in 1962 by D'Yvoire (3) by heating progressively a mixture of $Fe(PO_4)$ and $Fe(PO_3)_3$ to 950°C. This author only gives an unindexed X-ray powder diffraction pattern: JCPDS card no. 36-318 which actually is the only crystallographic reference for this compound.

In 1964, Remy and Boulé (5) indicated the existence of $Cr_4(P_2O_7)_3$ which, according to these authors, would be isotypic with $Fe_4(P_2O_7)_3$ prepared by D'Yvoire (3).

Later, in 1983, Schlesinger *et al.* (6) succeeded in the synthesis of single crystals of $V_4(P_2O_7)_3$ and $Cr_4(P_2O_7)_3$. Both compounds crystallize in the orthorhombic system (*Pbn2*₁ or *Pbnm*) with the following lattice parameters:

	a (Å)	b (Å)	c (Å)	S.G.
$V_4(P_2O_7)_3$	9.601(2)	21.425(5)	7.470(4)	Pbnm
$Cr_4(P_2O_7)_3$	9.38(1)	21.00(4)	7.26(2)	Pbnm

Finally, the structure of $V_4(P_2O_7)_3$ was determined by Palkina *et al.* (7) in the space group *Pmcn* with the cell parameters a = 7.443 Å, b = 9.560 Å, c = 21.347 Å.



In this structure, vanadium atoms occupy two 8(d) sites. Each vanadium sublattice (V(1) or V(2)) is characterized by the occurrence of V₂O₉ units made of two face-sharing VO₆ octahedra. These dimers are interconnected via the diphosphate groups.

At the same time, Modaressi (1) synthesized a single crystal of Fe₄(P₂O₇)₃. According to this author, Fe₄(P₂O₇)₃ crystallizes in an orthorhombic unit cell (*Pmnm*) with a = 7.389 Å, b = 21.337 Å, c = 9.517 Å. Nevertheless, all attempts to determine the structure have failed and the best fit to their data was obtained in the space group *Pmn*2₁ (with a structural arrangement close to that observed in V₄(P₂O₇)₃) but yielding the poor reliability factor R = 20%.

The present study clearly shows that the crystal structure of $Fe_4(P_2O_7)_3$ has a framework similar to that of $V_4(P_2O_7)_3$, but in a less symmetric monoclinic unit cell. In this paper, we also report on the magnetic properties of $Fe_4(P_2O_7)_3$ studied by bulk magnetization, Mössbauer spectrometry, and neutron diffraction experiments.

EXPERIMENTAL

 $Fe_4(P_2O_7)_3$ was prepared by firing, in an alumina crucible, the mixture $Fe(PO_3)_3 + 3FePO_4$, under dried oxygen, for 72 h at 940°C. In air, the resulting phosphate sets in a highly solid block which is difficult to grind (8).

The starting compounds were prepared by mixing aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$ and H_3PO_4 with the ratio $Fe/P = \frac{1}{3}$ and $\frac{1}{1}$ respectively. The solutions were evaporated to dryness and the residues were subsequently heated to $400^{\circ}C$ under nitrogen, and then at 900°C under oxygen for 24 h.

Single crystals were obtained by long annealing (15 days), in sealed silica tubes, within a gold crucible, under vacuum, at 900°C, with traces of FeCl₂ as mineralizer agent.

A single crystal ($\phi \sim 70 \,\mu\text{m}$) was selected for the structure determination. The data were collected on a Nonius CAD 4 automatic diffractometer at the Service Commun de Diffractométrie de l'Université Henri Poincaré-Nancy I.

Magnetic measurements were performed (between 4.2 and 300 K) on a MANICS magnetosusceptometer in magnetic field up to 1.6 T.

Neutron diffraction experiments were carried out at the Institut Laue Langevin (ILL), Grenoble. Several diffraction patterns were recorded with the one-dimensional curved multidetector D1b using a neutron wavelength of 2.520 Å, in the temperature range 120–1.7 K. Analysis of the patterns was performed by Rietveld profile refinements (9) using the software Fullprof (10).

The Mössbauer data were collected with a constant acceleration spectrometer with 1024 channels. Isomer shifts are reported with respect to α -iron at room temperature. The Mössbauer effect data were analyzed by using least-squares minimization techniques (11) to evaluate the hyperfine spectral parameters.

CRYSTAL STRUCTURE

(a) Structure Analysis

In the first step, a single crystal ($\phi \sim 70 \,\mu\text{m}$) was studied by conventional X-ray techniques (oscillating crystal and Weissenberg camera, Co K α). An orthorhombic unit cell of a = 7.389 Å, b = 21.337 Å, c = 9.517 Å (similar to those given in Ref. (1)) was deduced. The condition limiting possible reflections [(hol) with h + l = 2n] leads to three possible space groups: *Pmnm*, *Pmn2*₁, and *P2*₁*nm*.

In the second step, the crystal was mounted on an automatic diffractometer. Analysis of the intensities shows, beside the (h0l) with h + l = 2n condition previously observed, the additional extinction (0k0) with k = 2n + 1 which has been unambiguously confirmed by very long duration Weissenberg patterns.

This last condition implies the occurrence of a 2_1 screw axis parallel to *b*, which is incompatible with the orthorhombic groups *Pmnm*, *Pmn2*₁, and *P2*₁*nm*. Only the *P1* $2_1/n1$ space group fulfills all these constraints.

Thus, the structure of $Fe_4(P_2O_7)_3$ has been studied in the nonconventional monoclinic space group $P2_1/n$. The conditions for the data collection and the refinement of the structure are listed in Table 1. Absorption was neglected ($\mu r \ll 1$). Atomic scattering factors for Fe³⁺, P⁰, and O⁻ were taken from Ref. (12). All computer programs used were

 TABLE 1

 Summary of Data Collection and Structure Refinement

Molar mass (g.mol ⁻¹)	745.38
Crystal size (µm)	$\varphi \approx 70$
Symmetry	Monoclinic
a (Å)	7.389(2)
b (Å)	21.337(1)
c (Å)	9.517(2)
β(°)	90(1)
V (Å ³)	1500.4
Z	4
$\rho_{\rm cal} (\rm g.cm^{-3})$	3.3
Space group	$P2_1/n$
Radiation	ΜοΚα
Monochromator	Graphite
Scanning	$\theta - 2\hat{\theta}$
Take-off (°)	2.3
Record limits (°)	$\theta < 21$
Linear absorption coefficient $\mu(\text{cm}^{-1})$	24
Recorded intensities	1560
Recorded intensities with $\sigma(I)/I < 0.33$	1147
F(000)	1483
Number of parameters	146
Final R value	10%
Final $R_{\rm w}$ value	9%

TABLE 2Atomic Coordinates for Fe4(P2O7)3

Atom	x	У	Ζ
Fe(1)	0.0521(5)	0.2554(4)	0.7845(7)
Fe(2)	0.4644(8)	0.2593(3)	0.7901(10)
Fe(3)	0.4595(8)	0.0009(3)	0.2398(10)
Fe(4)	0.0582(8)	0.9964(4)	0.2427(10)
P(1)	0.2539(7)	0.2011(3)	0.0553(9)
P(2)	0.2514(7)	0.0627(3)	0.9744(10)
P(3)	0.2522(7)	0.0455(3)	0.5323(9)
P(4)	0.2440(8)	0.8591(4)	0.1543(11)
P(5)	0.2579(8)	0.1855(2)	0.5089(10)
P(6)	0.7572(8)	0.1112(6)	0.1706(9)
O(1)	0.264(2)	0.923(2)	0.232(2)
O(2)	0.259(2)	0.215(1)	0.656(1)
O(3)	0.248(3)	0.022(2)	0.103(2)
O(4)	0.226(2)	0.131(1)	0.029(2)
O(5)	0.245(2)	0.032(2)	0.377(1)
O(6)	0.259(1)	0.236(1)	0.910(2)
O(7)	0.939(3)	0.073(2)	0.199(2)
O(8)	0.274(2)	0.329(1)	0.750(1)
O(9)	0.572(2)	0.947(2)	0.110(2)
O(10)	0.592(3)	0.074(2)	0.193(1)
O(11)	0.594(2)	0.305(1)	0.923(2)
O(12)	0.913(2)	0.953(2)	0.110(2)
O(13)	0.588(2)	0.182(1)	0.817(2)
O(14)	0.923(3)	0.174(1)	0.803(2)
O(15)	0.923(2)	0.302(1)	0.931(2)
O(16)	0.211(2)	0.874(1)	0.003(1)
O(17)	0.952(2)	0.959(2)	0.392(1)
O(18)	0.948(2)	0.290(3)	0.621(1)
O(19)	0.322(3)	0.109(2)	0.537(1)
O(20)	0.101(3)	0.214(2)	0.129(3)
O(21)	0.381(2)	0.014(2)	0.621(1)

taken from Refs. (13, 14). The cell parameters were determined by least-squares refinements of the 20 values of 25 independent reflection-antireflections, measured for $2\theta > 17^{\circ}$:

a = 7.389(2) Å, b = 21.337(1) Å, c = 9.517(2) Å, and $\beta = 90(1)^{\circ}$.

The iron and phosphorus atomic positions have been obtained using the direct methods procedure (13). The oxygen atomic positions were determined, step by step, by difference Fourier synthesis. Due to the lack of data (very small crystal), we only refined a general temperature factor $(B_G = 0.58 \text{ Å}^2)$ yielding the final residual R = 0.10 $(R_w = 0.09)$. The atomic parameters are listed in Table 2 and the main interatomic distances and angles are given in Table 3. It is noteworthy that some P–O distances are very short. Despite many tests, we did not manage to correct these anomalies. However, it should be noted that similar short P–O distances were also observed in some phosphates and diphosphates (1.43 Å) (15, 16).

(b) Description

The mean feature of the structure of $Fe_4(P_2O_7)_3$ is the occurrence of Fe_2O_9 dimers made of face-sharing FeO_6 octahedra. Iron atoms are slightly off-centered in each octahedron in order to minimize the repulsive interactions between the common faces (Table 3). One observes two types of dimers: [Fe(1), Fe(2)] and [Fe(3), Fe(4)] with an Fe-Fe distance of 3.05 and 2.97 Å, respectively. The dimers are connected by $(PO_4)^{3-}$ entities yielding infinite (010) layers made of [Fe(1), Fe(2)] or [Fe(3), Fe(4)] iron planes. These layers are alternatively stacked along the screw axis through $(P_2O_7)^{4-}$ units (Fig. 1, see also Fig. 7). Hence, this structure is very similar to that of $V_4(P_2O_7)_3$ (7).

In the diphosphate units, some P–O distances remain short (Table 3), but the average values are comparable to the 1.536 Å value given by Corbridge (17). All the conformations are of staggered form. Furthermore, the P–O–P links

 TABLE 3

 Main Interatomic Distances (Å) and Angles (°)

	[FeO ₆] Octahed	Ira					
Fe(1)-O(18)	1.89(3)	Fe(3)-O(21)	1.80(2)				
Fe(1)-O(15)	1.96(2)	Fe(3)-O(9)	1.88(3)				
Fe(1)-O(6)	1.98(1)	Fe(3)-O(10)	1.89(4)				
Fe(1)-O(14)	1.99(2)	Fe(3)-O(3)	2.08(2)				
Fe(1)-O(2)	2.14(2)	Fe(3)-O(5)	2.16(2)				
Fe(1)-O(8)	2.29(2)	Fe(3)-O(1)	2.20(3)				
Fe(2)-O(11)	1.86(2)	Fe(4)-O(17)	1.81(2)				
Fe(2)-O(13)	1.90(2)	Fe(4)-O(12)	1.90(3)				
Fe(2)-O(20)	1.92(3)	Fe(4)-O(7)	1.90(4)				
Fe(2)-O(6)	1.96(2)	Fe(4)-O(3)	2.01(2)				
Fe(2)-O(8)	2.08(2)	Fe(4)-O(5)	2.03(2)				
Fe(2)-O(2)	2.20(2)	Fe(4)-O(1)	2.18(3)				
Fe(1)-Fe(2)	3.048(7)	Fe(3)-Fe(4)	2.967(8)				
[PO]] Tetrahedra							
P(1)-O(20)	1.36(3)	P(4)-O(14)	1.48(2)				
P(1)-O(4)	1.53(2)	P(4)-O(16)	1.49(2)				
P(1)-O(6)	1.57(2)	P(4)-O(13)	1.54(2)				
P(1)-O(18)	1.58(2)	P(4)-O(1)	1.56(4)				
$\langle P(1)-O \rangle$	1.51	$\langle P(4)-O \rangle$	1.52				
P(2)-O(12)	1.49(2)	P(5)-O(15)	1.45(2)				
P(2)-O(3)	1.50(3)	P(5)-O(11)	1.48(2)				
P(2)-O(9)	1.55(2)	P(5)-O(2)	1.53(2)				
P(2)-O(4)	1.56(2)	P(5)-O(19)	1.72(4)				
$\langle P(2)-O \rangle$	1.52	$\langle P(5)-O \rangle$	1.54				
P(3)-O(21)	1.44(2)	P(6)-O(10)	1.47(3)				
P(3)-O(19)	1.45(4)	P(6)-O(8)	1.49(2)				
P(3)-O(5)	1.51(2)	P(6)-O(7)	1.59(3)				
P(3)-O(17)	1.67(2)	P(6)-O(16)	1.70(1)				
$\langle P(3)-O \rangle$	1.52	$\langle P(6)-O \rangle$	1.56				
P(1)-O(4)-P(2)	162(1)	P(3)-O(19)-P(5)	142(2)				
P(4)-O(16)-P(6)	163(1)						



FIG. 1. Projection of the framework of $Fe_4(P_2O_7)_3$. (Top) Parallel to [100]. (Bottom) Parallel to [001].

are bent and the angles values are of 142, 162, and 163° for P(3)–O–P(5), P(2)–O–P(1), and P(6)–O–P(4), respectively (Fig. 1).

(c) Relationships among Iron Diphosphates

The analysis of the structures of $Fe_3(P_2O_7)_2$ (18) and $Fe_4(P_2O_7)_3$ shows certain similarities. Thus, in the latter compound, the sequence of dimers along the *a* axis

generates an empty prismatic site with triangular bases, similar to that occupied by the Fe^{2+} ion in $Fe_3(P_2O_7)_2$ (see Fig. 2). This observation suggests a structural relationship between these two compounds.

One can imagine the following mechanism. On the basis of two dimers "Fe1-Fe2_{octa}-empty prism-Fe1-Fe2_{octa}," the occupation of the prismatic site by Fe²⁺ ion and the departure of the Fe³⁺ ions of the two octahedra of the ends lead to the formation of the trimer Fe₃O₁₂ characteristic of Fe₃(P₂O₇)₂. However, in Fe₄(P₂O₇)₃, the vertical edges joining the triangular bases of the prism are generated by edges of PO₄ tetrahedra of the diphosphates groups. That supposes also a rearrangement of a part of the P₂O₇ subnetwork. This remark seriously complicates the considered process since it imposes a significant three-dimensional reorganization of the anions. The assumption is nevertheless tempting and it may appear significant to announce it.

MAGNETIC STUDY

(a) Susceptibility Measurements

The thermal variation of the reciprocal susceptibility $(1/\chi)$ of Fe₄(P₂O₇)₃ in an applied field value of 4930 G (Fig. 3a) shows antiferromagnetic behavior below $T_{\rm N} = 50(5)$ K.

Above 50 K, the compound is paramagnetic and the temperature dependence of $1/\chi$ obeys the Curie–Weiss law with the apparent Curie constant of 18.9 emu K⁻¹ per formula unit. This value corresponds to an apparent effective magnetic moment/iron atom of $\mu_{eff} = 6.14 \,\mu_B$ which is slightly higher than the value expected for Fe³⁺ (d^5) in a H.S. ground state. The Curie temperature $\theta_P = -73$ K is consistent with dominant antiferromagnetic interactions. These results agree with the previous data of Reiff and Torardi (19).



FIG. 2. Trimer in $Fe_3(P_2O_7)_2$ (18) and hypothetical one in $Fe_4(P_2O_7)_3$.



FIG. 3. (a) Temperature dependence of the inverse magnetic susceptibility of $Fe_4(P_2O_7)_3$. (b) $Fe_4(P_2O_7)_3$ magnetization versus applied field at 5 K.

At 5 K, the isotherm curve (Fig. 3b) evidences neither spontaneous magnetization nor a metamagnetic-like behavior.

(b) Neutron Diffraction Study

The neutron diffraction pattern at 120 K is characteristic of only nuclear scattering. The refined cell parameters $(R_{\rm B} = 0.11)$ are a = 7.386(2) Å, b = 21.298(5) Å, c = 9.492(2) Å, and $\beta = 90.03(6)^{\circ}$.

Due to the lack of experimental information as there are 93 variable parameters to determine from 57 independent neutron data, a full refinement was not possible. Therefore, using the set of nuclear parameters defined during the single-crystal X-ray study (Table 2), only the scale factor, the lattice, and half-width parameters were refined at 120 K. The observed and the calculated diffraction profiles at 120 K are given in Fig. 4a.

Below 50 K, additional lines characteristic of an antiferromagnetic ordering appear in the neutron diffraction patterns, in agreement with the magnetic measurements. The neutron diffraction pattern collected and calculated at 1.7 K is shown in Fig. 4b. All these new reflections can be indexed on the basis of the nuclear unit cell and obey the rule (*h0l*) with h + l = 2n + 1 (i.e., forbidden by the *n* glide plane). Moreover, it must be noted that some nuclear reflections have magnetic contributions to their intensities (Fig. 4c).

Let us recall that there are four independent iron sites (Table 2) and for each iron sublattice, there are four equivalent positions per unit cell. Iron atoms can be separated in two sets of positions labeled (Fe_{1,j}; Fe_{2,j}) and (Fe_{3,j}; Fe_{4,j}) corresponding to the two types of Fe₂O₉ dimers. For the notation Fe_{*i*,*j*}, i = 1, 4 corresponds to the four crystallographic iron sites and j = 1, 4 corresponds to the four equivalent positions, as indicated in Fig. 5.

All possible collinear models, in agreement with the loss of the glide plane, were tested.

Considering the small number of magnetic data, the magnetic moment components were constrained to be equal for the four independent iron sites. The best refinement corresponds to the following model:

—each iron sublattice (i) is antiferromagnetic,

—in each dimer [Fe(1), Fe(2)] and [Fe(3), Fe(4)] the iron atoms are antiferromagnetically coupled.

—the spin direction lies along the *c* axis.



FIG.4. Observed and calculated neutron diffraction patterns of $Fe_4(P_2O_7)_3$: (a) at 120 K, (b) at 1.7 K, (c) difference between the observed spectra collected at 120 and 1.7 K.



FIG. 5. Collinear arrangement of spin for antiferromagnetic ordering of Fe₄(P₂O₇)₃. The gray and white circles indicate opposite spin direction parallel to the *c* axis. Only Fe atoms (Fe₂O₉ dimers) are shown and referenced as *i*, *j*: *i* = 1 - 4; *j* corresponds to equivalent positions *x*, *y*, *z*; $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; -x, -y, -z; and $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$, respectively. The black bonds represent the 2.967 and 3.048 Å intradimer Fe-Fe distances.

The magnetic structure is represented in Fig. 5. At 1.7 K, the best refinement ($R_{\rm NUC} = 10.4\%$ and $R_{\rm MAG} = 7.2\%$) yields $\mu_{\rm Fe} = 4.55(5) \ \mu_{\rm B}$ (Fig. 4b).

The thermal dependence of the magnetic moment amplitude is shown in Fig. 6. The magnetic moment obeys the usual Brillouin-type variation versus temperature, leading to $T_{\rm N} = 57(2)$ K, in fair agreement with the previous bulk magnetization measurements.

(c) Mössbauer Study

Paramagnetic state (T > 55 K). The room temperature spectrum (Fig. 7) was fitted with four Lorentz-type symmetric quadrupole doublets, in agreement with the existence of the four crystallographic Fe sites.

The intensity of each doublet was constrained to be equal as well as the width of the peaks (I, Γ) . The refined values of the hyperfine parameters are given in Table 4. An attempt to analyze the spectrum with two symmetric quadrupole



FIG. 6. Thermal variation of the Fe^{3+} magnetic moment in $Fe_4(P_2O_7)_3$.



FIG. 7. Mössbauer spectra of $Fe_4(P_2O_7)_3$ obtained at 295 and 4.2 K.

doublets (i.e., orthorhombic cell) leads to too wide peaks ($\Gamma = 0.41 \text{ mm/s}$). This result consolidates the monoclinic structural model proposed in the present crystallographic study.

The isomer shifts (δ) are clearly indicative of high-spin Fe³⁺ ions in an octahedral oxygen crystal field. Let us recall that the usual values measured in oxides are, according to Menil (20), in the range 0.29–0.50 mm/s for Fe³⁺ in VI coordination. The high average value, 0.415 mm/s, observed here is not unexpected, as it has been well established by Gleitzer (8) that, thanks to the inductive effect, the Fe–O bond in phosphate is rather highly ionic.

The increasing quadrupole splitting values $\Delta = 0.40, 0.55, 0.77$, and 0.90 mm/s are clearly indicative of an Fe³⁺ ion in a highly distorted octahedral configuration (see Table 3). Examination of the Fe-O distances shows that the

TABLE 4Mössbauer Spectral Parameters for Fe4(P2O7)3 at 295 K

δ^a (mm/s)	Δ (mm/s)	Γ (mm/s)	I (%)
0.418	0.406	0.251	25
0.414	0.549	0.251	25
0.412	0.768	0.251	25
0.418	0.904	0.251	25
	δ^a (mm/s) 0.418 0.414 0.412 0.418	$\begin{array}{ccc} \delta^a & \Delta \\ (mm/s) & (mm/s) \\ \hline 0.418 & 0.406 \\ 0.414 & 0.549 \\ 0.412 & 0.768 \\ 0.418 & 0.904 \\ \hline \end{array}$	$\begin{array}{c cccc} \delta^a & \Delta & \Gamma \\ (mm/s) & (mm/s) & (mm/s) \\ \hline 0.418 & 0.406 & 0.251 \\ 0.414 & 0.549 & 0.251 \\ 0.412 & 0.768 & 0.251 \\ 0.418 & 0.904 & 0.251 \\ \hline \end{array}$

"Relative to room temperature α -iron foil. $\delta \pm 0.002$, $\Delta \pm 0.002$, $\Gamma \pm 0.002$.



FIG. 8. Interdimer Fe-O-P-O-Fe superexchange pathway in a (010) layer.

coordination (4 + 2) for Fe(1) and Fe(3) and (5 + 1) for Fe(2) and Fe(4) can be related to $\Delta = 0.40$, 0.55 and $\Delta = 0.77$, 0.90 mm/s, respectively.

Ordered state (T = 4.2 K). The Mössbauer spectrum of Fe₄(P₂O₇)₃ measured at 4.2 K is shown in Fig. 7. It has been fitted with four magnetic sextets of equal relative area and width of peak. The calculated hyperfine spectral parameters are given in Table 5. The hyperfine fields are rather similar, 56.0 and 54.4 T; these values are typical of an Fe³⁺ highspin ion close to the saturation state.

The values of the different isomer shifts remain close (0.567 to 0.580 mm/s) and their temperature dependence is in agreement with the second-order Doppler shift.

These results nicely explain the data obtained by Reiff and Torardi (19) on a topotactically prepared $Fe_4(P_2O_7)_3$ sample.

(d) Discussion

The magnetic structure of $Fe_4(P_2O_7)_3$ is characterized by the occurrence of antiferromagnetic Fe_2O_9 units building up infinite (010) layers via "O–P–O" connections (Fig. 8). These layers are stacked along the *b* axis and are connected, one to the others, by "O–P–O" and "O–P–O–P–O" links. To discuss the magnetic exchange interactions we have to consider two types of couplings: intra- and interdimers.

Interactions within the Fe_2O_9 groups. (1) The cationcation direct interactions are important since the cation separation, through the common face, is relatively small (mean distance Fe-Fe ≈ 3 Å). These interactions, occurring between two half-filled orbitals, are obviously antiferromagnetic, as the transferred electron must be antiparallel to the net spin at both ions (21).

(2) The cation-anion-cation interactions are characterized by Fe-O-Fe angles close to 90° (Table 6). Accordingly they are moderately antiferromagnetic, thanks to delocalization superexchange, and partly to correlation superexchange.

TABLE 5Mössbauer Spectral Parameters for Fe4(P2O7)3 at 4.2 K

Site	δ^a (mm/s)	2ε (mm/s)	<i>Н</i> (Т)	Γ (mm/s)	I (%)
s1	0.567	- 0.041	55.9	0.270	25
s2	0.570	-0.411	56.0	0.270	25
s3	0.570	-0.149	54.3	0.270	25
<i>s</i> 4	0.580	- 0.639	54.3	0.270	25

"Relative to room temperature α -iron foil. $\delta \pm 0.002$, $\Delta \pm 0.002$, $\Gamma \pm 0.002$.

STRUCTURE AND MAGNETIC PROPERTIES OF Fe₄(P₂O₇)₃

		,	TABLE 6			
Magnetic	Interactions	in	$Fe_4(P_2O_7)_3$	between	Trivalent	Iron

Interaction	Nature	Sign	n	Path	Angle Fe-O-Fe	Fe-Fe Distance
Fe(1)-Fe(2)	Direct	AF	1			3.05 Å
Fe(3)-Fe(4)	"	AF	1			2.97 Å
Fe(3)-O(3)-Fe(4)	Superexchange	AF	1		93°	
Fe(3)-O(5)-Fe(4)	"	AF	1		90°	
Fe(3)-O(1)-Fe(4)	"	AF	1		85°	
Fe(1)-O(2)-Fe(2)	"	AF	1		89°	
Fe(1)-O(8)-Fe(2)	"	AF	1		88°	
Fe(1)-O(6)-Fe(2)	"	AF	1		101°	
Fe(1)-O(18)-P(1)-O(20)-Fe(2)	Super	AF	2	3.81 Å, 122°		4.34 Å
$Fe(1)-O(18)-P(1)-O(6)_{f}-Fe(2)$	-superexchange	F	2	3.85 Å, 106°		4.76 Å
$Fe(1)-O(18)-P(1)-O(6)_{e}-Fe(1)$	Via P(1)	AF	2	3.87 Å, 106°		6.03 Å
$Fe(2)-O(20)-P(1)-O(6)_{f}-Fe(1)$		F	2	3.90 Å, 112°		4.86 Å
$Fe(1)-O(20)-P(1)-O(6)_{e}-Fe(2)$		AF	2	3.88 Å, 112°		6.04 Å
Fe(3)-O(9)-P(2)-O(12)-Fe(4)	Via P(2)	AF	2	3.78 Å, 12°		4.42 Å
$Fe(3)-O(9)-P(2)-O(3)_{f}-Fe(3)$		F	2	3.96 Å, 111°		4.60 Å
$Fe(3)-O(9)-P(2)-O(3)_{e}-Fe(4)$		AF	2	3.89 Å, 111°		5.81 Å
$Fe(4)-O(12)-P(2)-O(3)_{f}-Fe(4)$		F	2	3.91 Å, 107°		4.70 Å
$Fe(4)-O(12)-P(2)-O(3)_{e}-Fe(3)$		AF	2	3.98 Å, 107°		5.97 Å
Fe(3)-O(21)-P(3)-O(17)-Fe(4)	Via P(3)	AF	2	3.61 Å, 108°		4.42 Å
$Fe(3)-O(21)-P(3)-O(5)_{f}-Fe(3)$		F	2	3.96 Å, 121°		4.99 Å
$Fe(3)-O(21)-P(3)-O(5)_{f}-Fe(4)$		AF	2	3.83 Å, 121°		6.08 Å
$Fe(4)-O(17)-P(3)-O(5)_{e}-Fe(4)$		F	2	3.84 Å, 112°		4.97 Å
Fe(4)-O(17)-P(3)-O(5)-Fe(3)		AF	2	3.97 Å, 112°		6.24 Å
Fe(1)-O(14)-P(4)-O(13)-Fe(2)	Via P(4)	AF	2	3.89 Å, 111°		4.34 Å
$Fe(1)-O(14)-P(4)-O(1)_{e}-Fe(4)$		F	1	4.17 Å, 112°		5.44 Å
Fe(1)-O(14)-P(4)-O(1)-Fe(3)		AF	1	4.19 Å, 112°		6.65 Å
$Fe(2)-O(13)-P(4)-O(1)_{e}-Fe(3)$		F	1	$4.10 \text{ Å}, 110^{\circ}$		5.59 Å
Fe(2)-O(13)-P(4)-O(1)-Fe(4)		AF	1	4.08 Å, 110°		6.50 Å
Fe(1)-O(15)-P(5)-O(11)-Fe(2)	Via P(5)	AF	2	3.82 Å, 112°		4.34 Å
$Fe(1)-O(15)-P(5)-O(2)_{e}-Fe(2)$		F	2	4.16 Å, 113°		4.86 Å
$Fe(1)-O(15)-P(5)-O(2)_{e}-Fe(1)$		AF	2	4.10 Å, 113°		6.03 Å
Fe(2)-O(11)-P(5)-O(2)-Fe(1)		F	2	4.00 Å, 117°		4.76 Å
Fe(2)-O(11)-P5-O(2)-Fe(2)		AF	2	4.06 Å, 117°		6.04 Å
Fe(3)-O(10)-P(6)-O(7)-Fe(4)	Via P(6)	AF	2	3.79 Å, 114°		4.42 Å
Fe(3)-O(10)-P(6)-O(8)-Fe(1)		F	1	4.18 Å, 117°		5.26 Å
Fe(3)-O(10)-P(6)-O(8)-Fe(2)		AF	1	3.97 Å, 117°		6.35 Å
Fe(4)-O(7)-P(6)-O(8)-Fe(2)		F	1	3.98 Å, 106°		5.28 Å
$Fe(4)-O(7)-P(6)-O(8)_{f}-Fe(1)$		AF	1	4.19 Å, 106°		6.49 Å

Note. AF, antiferromagnetic; F, ferromagnetic; n, number of interactions per dimer; path, distance = Fe–O + O–Fe; angle = angle O–P–O; O_j , oxygen atom of shared faces.

Interactions between the Fe_2O_9 groups. As shown in Fig. 8, these interactions are assured by different supersuperexchange "Fe-O-P-O-Fe" bridges. In each (010) layer, when only the terminal oxygen atoms of the diphosphate groups are concerned (Table 6), namely in each [100] row, they are antiferromagnetic whereas a frustrated situation occurs from row to row via oxygen atoms of the shared faces.

Between the (010) layers, the exchange interactions are through Fe-O-P-O-Fe (Table 6) and Fe-O-P-O-Fe pathways (Fig. 1), which are the weakest as they call upon super-superexchange actions.

CONCLUSION

X-ray single-crystal and ⁵⁷Fe Mössbauer spectroscopy experiments allow us to conclude that $Fe_4(P_2O_7)_3$ crystallizes in the monoclinic space group $P2_1/n$. Its structure is characterized by the occurrence of face-sharing Fe_2O_9 units. The three-dimensional framework is built up from these dimers linked by bent diphosphates P_2O_7 (P-O-P ~ 156°). In fair agreement with Goodenough's rules, each dimer is antiferromagnetic whereas the "Fe-O-P-O-Fe" interdimer exchange interactions are essentially antiferromagnetic as classically observed in other iron diphosphates.

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REFERENCES

- 1. A. Modaressi, Univ. Thesis, Nancy, France, 1984.
- 2. M. Ijjaali, Univ. Thesis, Nancy, France, 1992.
- 3. F. D'Yvoire, Bull. Soc. Chim. Fr. 1224 (1962).
- B. Malaman, M. Ijjaali, R. Gerardin, G. Venturini, and C. Gleitzer, Eur. J. Solid State Inorg. Chem. 29, 1269 (1992).
- 5. P. Remy and A. Boulé, C. R. Acad. Sc. Paris 258, 927 (1964).
- K. Von Schlesinger, B. Ziemer, W. Hanke, and G. Ladwig, Z. Anorg. Allg. Chem. 500, 104 (1983).
- K. K. Palkina, S. I. Maksimova, N. T. Chibiskova, K. Schlesinger, and G. Ladwig, Z. Anorg. Allg. Chem. 529, 89 (1985).
- 8. C. Gleitzer, Eur. J. Solid State Inorg. Chem. 28, 77 (1991).

- 9. H. M. Rietveld, J. Appl. Crystallogr. 2, 65 (1969).
- J. Rodriguez-Carvajal, Fullprof Program, Laboratoire Leon Brillouin, 1998.
- 11. G. Le Caer, Private communication.
- 12. J. A. Ibers and W. C. Hamilton, "International Tables for X-Ray Crystallography," Vol. 4. Kynoch, Birmingham, 1976.
- G. Sheldrick, Shelx 76, Program for Crystal Structure Determination, Univ. Cambridge, 1976.
- A. Altomare, G. Cascarano, C. Giacovazo, and D. Viterbo, Acta Crystallogr. A 47, 744 (1991).
- 15. C. Calvo and P. K. L. Au, Can. J. Chem. 47, 3409 (1969).
- 16. A. G. Nord and P. Kierkegaard, Chem. Scr. 15, 27 (1980).
- 17. D. Corbridge, Bull. Soc. Fr. Miner. Crist. 94, 271 (1971).
- M. Ijjaali, G. Venturini, R. Gerardin, B. Malaman, and C. Gleitzer, Eur. J. Solid State Inorg. Chem. 28, 983 (1991).
- 19. W. M. Reiff and C. C. Torardi, Hyper. Interact. 53, 403 (1990).
- 20. F. Menil, J. Phys. Chem. Solids 46, 763 (1985).
- J. B. Goodenough, "Magnetism and the Chemical Bond." Interscience Publishers, New York, 1966.