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Crystal Structure of a New FeP_4 Modification

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In addition to monoclinic α-FeP_4 (space group $P2_1/c$, $a = 4.619$, $b = 13.670$, $c = 7.002$ Å, $\beta = 101.48°$, $Z = 6$) and orthorhombic β-FeP_4 (space group $C222_1$, $a = 5.005$, $b = 10.212$, $c = 5.530$ Å, $Z = 4$), a third modification, γ-FeP_4, has been synthesized and its structure determined from a single-crystal X-ray diffraction study. γ-FeP_4 crystallizes in monoclinic symmetry (space group $C2/c$, $a = 5.0543(7)$, $b = 10.407(2)$, $c = 11.069(2)$ Å, $\beta = 91.14(1)°$, $Z = 8$). The structure refinement was conducted with 560 unique structure factors yielding a final R value of 0.026, 49 variables being taken into account. Like the other MP_4 phases, the cations are octahedrally coordinated, and the phosphorous atoms are tetrahedrally surrounded by Fe and P atoms. From atomic bond considerations and ionic radii calculations, a low-spin d^6 configuration is inferred for γ-FeP_4, and no Fe–Fe bond is found, in agreement with conclusions drawn for α- and β-FeP_4. The γ-FeP_4 structure, which can be written as the sequence of planes p'o'po, p'o'po, . . . in the Rühl and Jeitschko symbolism, can be described as constituted of infinite zigzagging chains of (FeP_6) octahedra sharing only edges. Three such octahedra constitute the linear units of the phase, compared to two and four in CrP_4 and 6-MnP_4. Interatomic distances found in γ-FeP_4 are identical, within error, to those of the two other iron tetraphosphite modifications.

Introduction

It has been recently shown that semiconducting transition metal phosphides could be promising materials for optoelectronics and solar energy conversion (*1*). New syntheses carried out in the iron–phosphorus system led recently to the preparation of a new iron tetraphosphide γ-FeP_4 (*2*). Preliminary X-ray study indicates that the phase crystallizes with monoclinic symmetry (*2*) ($C2/c$ space group), with the following powder spectra refined cell parameters: $a = 5.0543(7)$, $b = 10.407(2)$, $c = 11.069(2)$ Å, $\beta = 91.14(1)°$, $V = 582.1(3)$ Å^3, $Z = 8$. This paper describes the structure determination of γ-FeP_4 and compares the crystal array of this new phase with that of the two other α- and β-FeP_4 iron tetraphosphides and some MP_4 transition metal compounds.

Experimental

To obtain γ-FeP_4 single crystals, the following preparation procedure was used (*2*).

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H_2-reduced iron powder (60-mesh Ventron m5N) and red phosphorus (Hoechst t6N) in the ratio 1:4 were heated in evacuated (10^{-5} mbar) and sealed quartz ampoules (diameter = 28 mm; length = 450 mm) in the presence of bromine (0.1 mg/cm^3). The red phosphorus was kept at 800 K and the iron powder at 1000 K for 30 days. Crystals as large as 1 mm were obtained. Semiquantitative microprobe analysis performed on single crystals indicated the new phase to be a phosphorus-rich iron compound and the crystal structure determination was done assuming a FeP_4 stoichiometric composition. Subsequent successful structure refinement completely confirmed that assumption (see below). Microscopic observations of γ-FeP_4 crystals clearly showed a systematic twinning of the samples. Since the study of that behavior was not in the scope of the present work, we systematically tried to separate the twinned crystals mechanically in order to obtain a single-crystal sample. After many attempts, this was finally achieved. The symmetry and parameters were determined on a CAD4 diffractometer. Because the crystal did not show any well-formed face, and because of the low absorption factor (70.4 cm^{-1}), no absorption correction was made. Table I gathers the main crystallographic and refinement data related to the structure determination.

TABLE I

γ-FeP_4 CRYSTALLOGRAPHIC DATA AND PARAMETERS OF THE X-RAY DATA COLLECTION AND REFINEMENT

Physical, crystallographic, and analytical data

Formula: FeP_4; molecular weight: 179.74
Crystal symmetry: monoclinic; space group: $C2/c$
Cell parameters (293 K):
a = 5.0543(7) Å; b = 10.407(2) Å; c = 11.069(2) Å
β = 91.14(1)°
V = 582.1(3) Å^3, Z = 8
Density: ρ_{cal} = 4.102
Absorption factor: $\mu(\lambda MoK_\alpha)$, 70.4 cm^{-1}
Crystal size: ≈0.020 × 0.020 × 0.020 mm^3

Data collection

Temperature: 293 K; radiation: MoK_α
Monochromator: oriented graphite (002); scan mode: $\omega/2\theta$
Recording angle range: 5–30°; scan angle: 0.85 + 0.35 tan θ
Value determining the scan speed:
SIGPRE: 0.85; SIGMA: 0.05; VPRE: 20°/min; T_{max} = 60 sec
Standard reflection: 030, $1\bar{2}\bar{1}$, $\bar{1}25$; periodicity: 3600 sec

Refinement conditions

Utilized reflections: 560 with $I > 3\sigma(I)$
Refined parameters: 49
Reliability factors: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$
$R_w = [\Sigma_w(|F_o| - |F_c|)^2/wF_o^2]^{1/2}$

Refinement results

R = 0.026, R_w = 0.031
Extinction coefficient: E_c = 0.37(3) × 10^{-5}
Difference Fourier maximum peak intensity; 0.6(1) e^-/Å^3

Structure Refinement

Programs used belonged to the SDP-PLUS package (1982 version) distributed by ENRAF–NONIUS and written by Frenz (*3*). Iron atomic positions were deduced from the Patterson map. A series of Fourier and Fourier difference maps helped introduce the remaining atoms. The refinement by a full-matrix least-squares method using scattering factors for neutral atoms corrected for anomalous dispersion and with isotropic temperature factors gave the reliability factor value of R = 0.040 and R_w = 0.052. Introduction of anisotropic temperature factors led then to R = 0.026 and R_w = 0.031, the extinction coefficient being equal to 0.37(3) × 10^{-5}. Table II lists the final fractional coordinates of the six independent atoms of the cell and their temperature factors.[1]

[1] See NAPS document No. 04470 for 3 pages of observed and calculated structure factors. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in

TABLE II

POSITIONAL PARAMETERS[a] AND THEIR ESTIMATED STANDARD DEVIATIONS AND REFINED TEMPERATURE FACTOR EXPRESSIONS[b]

Atom	Site	X	Y	Z	B_{eq} (Å^2)
Fe(1)	4(d)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	0.24(1)
Fe(2)	4(e)	0	0.07601(8)	$\frac{1}{4}$	0.22(1)
P(1)	8(f)	0.2997(2)	0.2328(1)	0.2921(1)	0.34(2)
P(2)	8(f)	0.2001(2)	0.4275(1)	0.21573(9)	0.32(2)
P(3)	8(f)	0.0396(2)	0.0926(1)	0.04951(9)	0.32(2)
P(4)	8(f)	0.0608(2)	0.3973(1)	0.02394(9)	0.31(2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	0.0021(3)	0.00012(6)	0.00091(5)	0.000(2)	0.000(2)	−0.00005(9)
Fe(2)	0.0019(2)	0.00018(6)	0.00080(5)	0	0.0000(2)	0
P(1)	0.0036(3)	0.00034(7)	0.00103(6)	−0.0002(3)	−0.0004(2)	0.0001(1)
P(2)	0.0024(3)	0.00048(7)	0.00106(6)	−0.0004(3)	0.0000(2)	−0.0000(1)
P(3)	0.0026(3)	0.00045(7)	0.00101(6)	0.0005(3)	0.0003(2)	−0.0001(1)
P(4)	0.0027(3)	0.00045(7)	0.00096(6)	−0.0005(3)	0.0000(2)	−0.0001(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parmeter, defined as,
$B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j B_{ij} \mathbf{a}_i \mathbf{a}_j$.

[b] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Structural Results and Discussion

Table III gathers the main interatomic distances and angles encountered in the γ-FeP_4 structure, which is shown in two different projections in Figs. 1 and 2. The iron atoms are approximately octahedrally surrounded by phosphorus atoms and the phosphorus atoms are tetrahedrally coordinated, half of them by two metal and two pnictogen atoms and the other half by one metal and three pnictogen atoms. The phosphorus anions form two-dimensional sheets of condensed puckered ten-member rings.

There exist essentially two ways to describe the TX_4 compounds (T = transition metal, X, = P, As). The first one analyzes the puckered two-dimensional network T_nX_{4n} of the structural stacking and is applicable to η-MnP_4, CrP_4, and β-FeP_4. The second one studies the various connections occurring between (TX_6) octahedra and consequently the associated pnictogen network. Since γ-Fep_4 can be described either way, two structural descriptions are given below.

Although presenting a purely tridimensional character, γ-FeP_4 can also be described as resulting from the stacking of Fe_nP_{4n} sheets made of [FeP_4] pentagons and [Fe_2P_4] hexagons (Fig. 3). Four such slabs Fe_nP_{4n}, having only slight differences in an-

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TABLE III

MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN (FeP_6), (P_3Fe_2), AND (P_4Fe) POLYHEDRA OF γ-FeP_4 (ESD AND NUMBER OF BONDS AND ANGLES BETWEEN BRACKETS)

Fe(1)–Fe(2)	3.520(1)		
P(1)	2.326(1) (×2)	P(1) –Fe(1)–P(3)	77.63(3) (×2), 102.37(4) (×2)
P(3)	2.257(1) (×2)	P(1) –Fe(1)–P(4)	88.58(3) (×2), 91.42(3) (×2)
P(4)	2.207(1) (×2)	P(3) –Fe(1)–P(4)	89.00(4) (×2), 91.00(4) (×2)
Fe(2)–P(1)	2.268(1) (×2)	P(1) –Fe(2)–P(1)	88.06(6) (×1)
P(2)	2.193(1) (×2)	P(1) –Fe(2)–P(3)	79.22(4) (×2)
P(3)	2.238(1) (×2)	P(2) –Fe(2)–P(3)	98.70(4) (×2)
		P(2) –Fe(2)–P(3)	87.56(4) (×2)
		P(1) –Fe(2)–P(2)	90.82(4) (×2)
		P(1) –Fe(2)–P(3)	94.37(4) (×2)
		P(2) –Fe(2)–P(2)	90.38(6) (×1)
Mean d_{Fe-P} = 2.248			
P(1)–Fe(1)	2.326(1)	Fe(1)–P(1) –Fe(2)	100.03(4)
Fe(2)	2.268(1)	Fe(1)–P(1) –P(2)	105.95(5)
P(1)	2.244(2)	P(2) –P(1) –P(1)	121.26(4)
P(2)	2.248(1)	Fe(1)–P(1) –P(1)	121.72(7)
		Fe(2)–P(1) –P(2)	115.25(5)
		P(1) –P(1) –P(2)	92.37(4)
P(2)–Fe(2)	2.193(1)	Fe(2)–P(2) –P(1)	114.88(5)
P(1)	2.248(1)	Fe(2)–P(2) –P(2)	125.77(4)
P(2)	2.174(2)	Fe(2)–P(2) –P(4)	117.73(4)
P(4)	2.245(1)	P(1) –P(2) –P(2)	94.14(4)
		P(1) –P(2) –P(4)	107.06(5)
		P(2) –P(2) –P(4)	93.01(6)
P(3)–Fe(1)	2.257(1)	Fe(1)–P(3) –Fe(2)	103.11(4)
Fe(2)	2.238(1)	Fe(1)–P(3) –P(3)	113.24(7)
P(3)	2.249(2)	Fe(1)–P(3) –P(4)	118.22(5)
P(4)	2.193(1)	Fe(2)–P(3) –P(3)	113.48(7)
		Fe(2)–P(3) –P(4)	118.11(5)
		P(3) –P(3) –P(4)	90.99(6)
P(4)–Fe(1)	2.207(1)	Fe(1)–P(4) –P(2)	114.85(4)
P(2)	2.245(1)	Fe(1)–P(4) –P(3)	130.32(5)
P(3)	2.193(1)	Fe(1)–P(4) –P(4)	115.72(6)
P(4)	2.283(2)	P(2) –P(4) –P(3)	93.96(5)
		P(2) –P(4) –P(4)	99.60(6)
		P(3) –P(4) –P(4)	96.61(6)
Mean d_{P-P} = 2.232			

gles and interatomic distances, are needed to constitute the basic cell. Using Rühl and Jeitschko symbolism (5), γ-FeP_4 can be described as the sequence of planes p′o′po, p′o′p. . . . This is to be compared to the stacking sequence of the five other MP_4 structures for which such a symbolism can be used. They are CrP_4 (oo′, oo′, . . .), 2-MnP_4 (pp, pp, . . .), 6-MnP_4 (ppop′p′o′, ppop′p′o′, . . .), 8-MnP_4 (pppp, p-p-p-p,

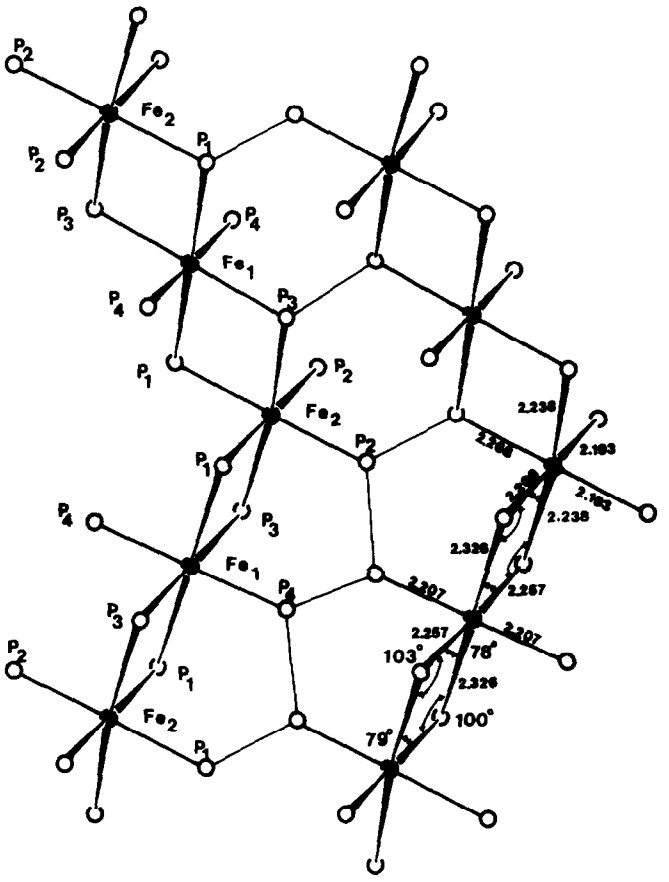

FIG. 1. Perspective drawing of the γ-FeP_4 structure (ORTEP). The right side gives some Fe–P distances and shows the distorted angle which allows cation separation.

pppp, p-p-p-p, . . .) and β-FeP_4 (o-o, o-o, . . .).

Although this symbolism allows one to ascertain and characterize the original structural nature of these compounds, it does not provide any information on the particular way the $[MP_6]$ octahedra of neighboring sheets share edges or corners.

As can be observed on Figs. 1 and 2, the new phase γ-FeP_4 exhibits infinite zigzagging chains of octahedra sharing only edges. These chains are made of linear units of three octahedra. This type of arrangement is to be compared to that encountered in CrP_4 (*4*) and 6-MnP_4 (*5*), where the linear modules are respectively of two and four octahedra. In 2-MnP_4 (*6*), the edge-sharing octahedra constitute infinite linear chains.

In the three phases, CrP_4, 6-MnP_4, and 2-MnP_4, the $[MP_6]$ octahedral groups share exclusively edges, giving short M–M distances and allowing cation–cation bonds, with Mn–Mn pairs, for example, in 6-MnP_4 (*5*) and 2-MnP_4 (*6*).

The γ-FeP_4 structure differs from that of the high-pressure β modification, in which the $[FeP_6]$ octahedra share only corners, and from that of α-FeP_4 (*8*), in which the $[FeP_6]$ groups share edges and corners.

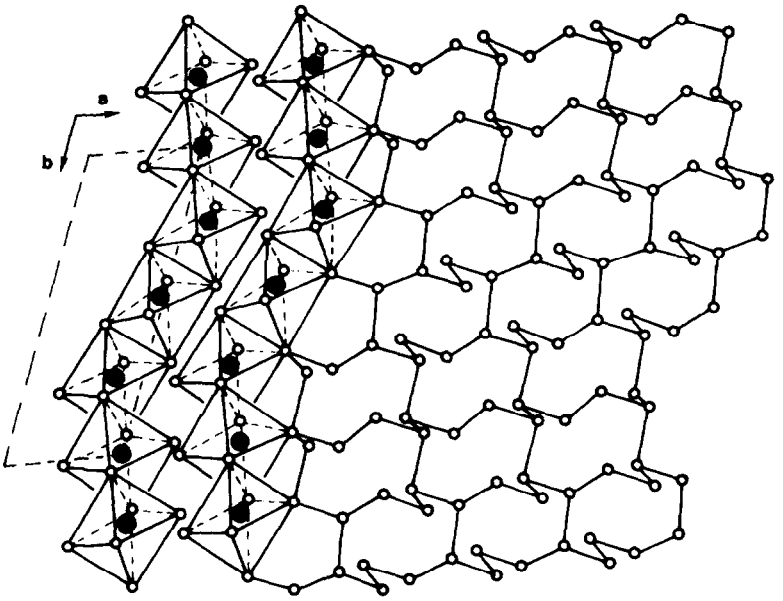

FIG. 2. Perspective drawing of γ-FeP_4 structure (ORTEP) showing the edge-sharing octahedra and their linear arrangement of $[FeP_6]_3$ units.

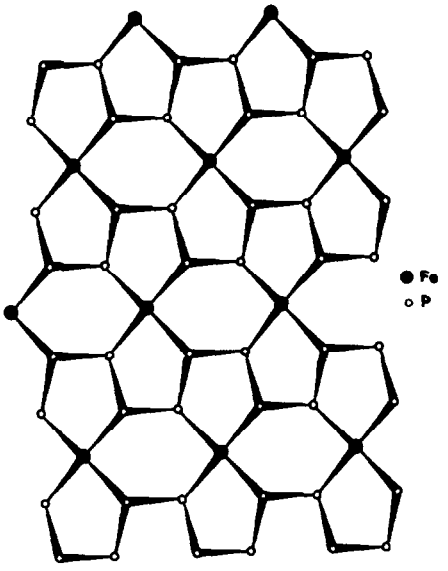

FIG. 3. The puckered sheet, made of (Fe_2P_4) hexagons and (FeP_4) pentagons, considered as a building plane of γ-FeP_4.

If one takes into account two valence electrons for each Fe–P and P–P bond and if one attributes these electrons to the phosphorus polyanion of the structure, a formal charge of +2 is found for iron (*8*). As demonstrated for the α-FeP_4 modification (*9*), iron can be assumed to have, in γ-FeP_4, a low-spin d^6 configuration and hence the phase is diamagnetic. This would imply unpaired iron cations, and indeed the shortest Fe^{2+}–Fe^{2+} distance is 3.520(1) Å, too long for any intercationic link. The structure keeps the iron ions well separated through the elongation of the Fe(1)–P–Fe(2) angles between the $[FeP_6]$ octahedra (see Fig. 1), inducing strong distortion in the structure (Table III). This structure feature was first pointed out by Jeitschko and Braun (*8*) in α-FeP_4.

Further evidence of the iron electronic configuration can also be deduced from the interatomic distances. If one considers the mean Fe–P bond lengths of the three FeP_4 structures, very similar values are observed, implying the same electronic ar-

TABLE IV

OBSERVED MEAN METAL–PHOSPHORUS DISTANCES IN SOME FIRST-ROW TRANSITION METAL TETRAPHOSPHIDES[a]

	Atomic distances and radii			
			$r_{M^{2+}}$ (Å)	
Compounds	Mean d_{M-P} (Å)	$r_{M^{2+}}$ (Å)	Low spin	High spin
CrP_4	2.336	0.70	0.73	0.80
2-MnP_4	2.273	0.63		
6-MnP_4	2.275	0.63	0.67	0.83
8-MnP_4	2.282	0.64		
α-FeP_4	2.259	0.62		
β-FeP_4	2.249	0.61	0.61	0.78
γ-FeP_4	2.248	0.61		

[a] Cationic radii were calculated using r_P = 1.64 Å (see text) and compared to that of the same cations in low-spin and high-spin configurations as found in halogenides and chalcogenides (from (*10*)).

rangement for Fe^{2+} (Table IV). Considering a low-spin cationic radius of 0.61 Å for Fe^{2+} as given by Shannon and Prewitt (*10*), an ionic radius of 1.64 Å can be calculated for phosphorus. This latter value yields radii of 0.63 and 0.70 Å, respectively, for Mn^{2+} and Cr^{2+} in MnP_4 and CrP_4 (Table IV), compared with the values of 0.67 and 0.73 Å for the same ions in low-spin configuration in chalcogenides according to the above reference. All these results are self-consistent and indicate the structure homogeneity of the three FeP_4 compounds as well as that of the MP_4 family (M = first-row transition metal). They are in agreement with bonding considerations developed by Jeitschko *et al.* (*4, 5, 8, 11*).

Conclusion

The new monoclinic γ-FeP_4 compound presents a structure based on edge-sharing (FeP_6) octahedra. From that point of view, it resembles other tetraphosphides of first-row transition metals that are also built in a similar way, namely CrP_4, 2-MnP_4, and 6-MnP_4. γ-FeP_4 differs from α- and β-FeP_4, which are built through corner sharing in the latter and through corner and edge sharing in the former. As far as bonding is concerned, however, γ-FeP_4 looks very much like the two other iron tetraphosphide compounds with isolated iron ions Fe^{2+} in the low-spin configuration ($t_{2g}^6 e_g^0$), implying diamagnetic behavior. This feature constitutes an important difference between the MnP_4 and CrP_4 compounds, for instance, in which metal–metal bonds are observed between adjacent octahedra. As found before, this property is related to the cation t_{2g} orbital filling state since, in the case of the FeP_4 phases, Fe^{2+} in $t_{2g}^6 e_g^0$ configuration cannot exchange Fe–Fe bonds through the octahedral edges. γ-FeP_4 structure supports and conclusions of previous studies made on related materials and polymorphs and provides a new example of polyhedral combination in the tetraphosphide family.

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