

## Occurrence of a Monoclinic Distortion in $\beta$ -Fe<sub>2</sub>PO<sub>5</sub>

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### Abstract

The structure of the mixed valence iron oxyphosphate  $\beta$ -Fe<sub>2</sub>PO<sub>5</sub> has been reinvestigated using powder synchrotron X-ray data. A previous study based on the similarity with the powder diagrams of NiCrPO<sub>5</sub> concluded that the structure existed in a tetragonal cell (*I4<sub>1</sub>/amd*). In this space group both Fe atoms, Fe<sup>2+</sup> and Fe<sup>3+</sup>, are sharing the same crystallographic site and, therefore, cannot be distinguished. Parts of the pattern have been measured at high resolution on the LURE D23 powder station. The instrumental resolution there clearly shows the splitting of some Bragg peaks. Among the subgroups of *I4<sub>1</sub>/amd*, the monoclinic group *I2/a* permits a description of the spectra if the twofold *b'* of the new unit cell is chosen as the diagonal of the square base of the tetragonal cell. A Rietveld refinement was then performed against the full powder diffraction diagram. This reveals two iron sites with slightly different Fe—O distances. Finally, study as a function of temperature shows a monoclinic to tetragonal transition above 415 K, which may be related to a magnetocrystalline effect at  $T_N = 408$  K.

### 1. Introduction

Synchrotron radiation allows high-resolution powder diffraction experiments as well as high intensity measurements, whilst keeping satisfactory resolution. These qualities have been used to precisely determine the crystal structure of  $\beta$ -Fe<sub>2</sub>PO<sub>5</sub>.

As a mixed valent iron compound, the oxyphosphate Fe<sub>2</sub>(PO<sub>4</sub>)O is well suited to investigate electronic exchange between the two cations. In this work we are concerned with the structure of the  $\beta$ -polymorph (low-temperature phase) of Fe<sub>2</sub>PO<sub>5</sub>. The other polymorph,  $\alpha$ -Fe<sub>2</sub>PO<sub>5</sub>, is orthorhombic (space group *Pnma*) with iron located on two different crystallographic sites separated by a distance of 2.92 Å (Modaresi, Courtois, Gerardin, Malaman & Gleitzer, 1981). For this latter compound a

study (Warner, Cheetham, Cox & Von Dreele, 1992) using magnetic neutron and resonant X-ray powder diffraction confirmed the presence of Fe<sup>2+</sup> on one site and Fe<sup>3+</sup> on the other.

The structure of  $\beta$ -Fe<sub>2</sub>PO<sub>5</sub> has been described by assuming an isomorphous structure to NiCrPO<sub>5</sub> and powder diffraction photographs (Ech-Chahed, Jeannot, Malaman & Gleitzer, 1988). Later, the structure was confirmed by a diffraction experiment on a small (25 µm) single crystal (Ijjaali *et al.*, 1990). The two studies led to a tetragonal cell [space group *I4<sub>1</sub>/amd*, with  $a_t = 5.3360(7)$  and  $c_t = 12.457(2)$  Å] where:

(i) iron occupies only one crystallographic site [(8*d*)] in rows of face-sharing FeO<sub>6</sub> octahedra.

(ii) The Fe—Fe distance (2.67 Å) is the shortest known in an oxygenated compound of iron (for example, Fe—Fe 2.97 Å in Fe<sub>3</sub>O<sub>4</sub>) and this is an ideal situation for a theoretical treatment of the electron transfer Fe<sup>2+</sup>—Fe<sup>3+</sup>.

However, despite the good reliability index obtained on the single-crystal data ( $wR = 3.6\%$ ), powder diffraction data of a well crystallized sample ( $\beta$ -Fe<sub>2</sub>PO<sub>5</sub> annealed at 873 K under vacuum for 1 month) recorded on a curved detector INEL CPS 120 show splitting of some peaks and broadening of others. This cannot be explained in the tetragonal model proposed earlier; to go further, several peaks were recorded using the synchrotron beam of DCI (LURE), at high resolution so as to be able to describe their profiles and in a new crystal system. Then a more complete diffraction pattern was recorded to refine the structure. Finally, this work was completed by an X-ray study as a function of temperature. This paper reports these results and findings.

### 2. High-resolution measurements

Selected Bragg peaks at low angles [(004)<sub>t</sub>, (112)<sub>t</sub> and (103)<sub>t</sub>, for tetragonal setting] were recorded on the D23 beamline at the DCI synchrotron of LURE (Orsay,

France).\* The wavelength (1.79 Å) was extracted from the white beam by means of a double Si(111) monochromator; a third Ge(111) crystal analysed the diffracted beam. This setup (Bessière, Bessenay, Frouin, Jouvin & Lefebvre, 1987; Elkaim *et al.*, 1992) adds only a weak instrumental broadening (FWHM < 0.025° 2θ), which permits a good separation of neighbouring peaks and a sensitive evaluation of sample peak width. This effect is clearly shown in Fig. 1 where the (103)<sub>t</sub> and (112)<sub>t</sub> lines split up in two and three peaks, whereas the (004)<sub>t</sub> reflections remains single and narrow. This splitting at low angles allows an easier understanding of the cell deformation. No orthorhombic setting explains this splitting, therefore, all the peaks were indexed in the monoclinic system. The resulting indexation led to the *I2/a* space group, which is a subgroup of *I4<sub>1</sub>/amd* (with the monoclinic *b* axis along the diagonal of the tetragonal square base and keeping one of the *d* mirrors which becomes *a*) and reproduces the observed sequence of lines as well as the space group extinctions. The transformation from the tetragonal cell to the monoclinic cell is given by

$$\begin{aligned} a_m &= \frac{1}{2}a_t - \frac{1}{2}b_t + \frac{1}{2}c_t \\ b_m &= -a_t - b_t \\ c_m &= \frac{1}{2}a_t - \frac{1}{2}b_t - \frac{1}{2}c_t. \end{aligned}$$

This leads to the starting parameters  $a_m = 7.282$ ,  $b_m = 7.5462$ ,  $c_m = 7.282$  Å and  $\beta = 117.588^\circ$ . After the

\*The numbered intensity of each measured point on the profile has been deposited with the IUCr (Reference: HE0141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Rietveld refinement (see below), the new parameters are  $a_m = 7.2956(7)$ ,  $b_m = 7.5605(7)$ ,  $c_m = 7.2512(7)$  Å and  $\beta = 117.368(2)^\circ$ , which corresponds to a weak distortion of the tetragonal cell.

### 3. Structure refinement

Since the high-resolution data set is not sufficient (only a few lines collected) for a structure refinement, a full diagram (13 < 2θ < 100°) was recorded on the LURE-WDIF4C wiggler beam line. For this instrument, the wavelength [1.1970(1) Å] is selected by a double Si(111) monochromator and an angular resolution of 0.08° 2θ is obtained using Soller slits. During the experiment the sample was rotated to minimize preferred orientation effects. Data were collected in less than 6 h with a step size of 0.02° 2θ and a counting time of 4 s per point.

Analysis of these data was carried out with the Rietveld program XND (Berar & Garnier, 1992). Profiles were described by a Voigt peak-shape function and the background was estimated by interpolation between points for which the height is refined. Neutral atom scattering factors (*International Tables for X-ray Crystallography*, 1994, Vol. 4) were used and a polarization factor of 0.95 applied. Additional lines from impurities appeared in the diagram; the main reflections of α-Fe<sub>2</sub>O<sub>3</sub>, α-Fe<sub>2</sub>PO<sub>5</sub> and Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> were identified but a fourth unknown compound also appears to be present. These additional lines were "removed" from the diagram by a separate peak fitting procedure. Details of the refinement and the atomic parameters are given in Tables 1 and 2, whilst the observed and calculated diagrams are shown in Fig. 2. It is worth noting that the calculated standard deviations given in the tables are underestimates and that a better estimate of the errors can be obtained by multiplying them by a factor  $f = 1.53$  due to correlations between adjacent points of the diagram (Berar & Lelann, 1991).

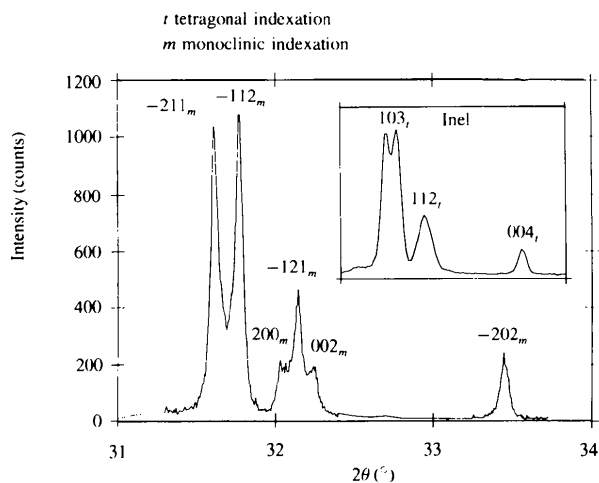


Fig. 1. Synchrotron and conventional X-ray diffraction profiles of selected peaks.

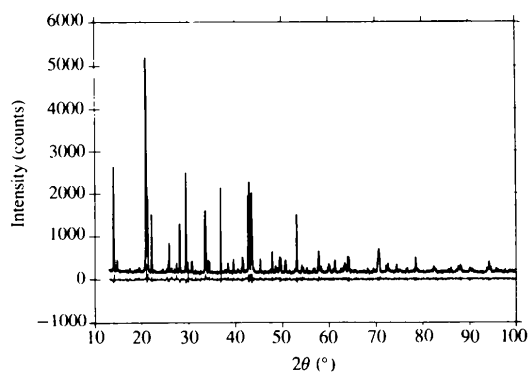


Fig. 2. Plot of the observed, calculated and difference intensities from the Rietveld refinement.

Table 1. Rietveld refinement parameters

Compound	$\beta$ -Fe <sub>2</sub> PO <sub>5</sub>
Space group	$I2/a$
$a$ (Å)	7.2956 (7)
$b$ (Å)	7.5605 (7)
$c$ (Å)	7.2512 (7)
$\beta$ (°)	117.368 (2)
$V$ (Å <sup>3</sup> )	355.2
$Z$	4
$\lambda$ (Å)	1.197
Angular domain (°)	$13 \leq 2\theta \leq 100$
Number of points	4352
Number of reflections	324
Total number of parameters	59
Number of structural parameters	18
$R_{wp}$	0.079
$R_p$	0.061
$R_{Bragg}(I)$	0.052
$R_F$	0.058
$R_{exp}$	0.063

Table 2. Fractional coordinates and isotropic thermal parameters (Å<sup>2</sup>), with standard deviations in parentheses

Position	Symmetry	$x$	$y$	$z$	$B$
Feb 4( <i>b</i> )	$\bar{1}$	0	1/2	0	0.55 (5)
Fec 4( <i>c</i> )	$\bar{1}$	3/4	1/4	1/4	0.69 (5)
O1a 8( <i>f</i> )	1	0.561 (1)	0.756 (1)	-0.060 (1)	0.20 (6)
O1b 8( <i>f</i> )	1	0.293 (1)	0.490 (1)	0.687 (1)	0.20 (6)
O2a 4( <i>e</i> )	2	3/4	0.3675 (15)	0	0.21 (14)
P 4( <i>e</i> )	2	1/4	0.1244 (6)	0	0.12 (6)

#### 4. Discussion

The main result of this study is that the Fe atoms are lying on two different sites [4(*b*) and 4(*c*)] in the monoclinic unit cell. However, as shown by the interatomic distances and angles listed in Table 3, one can see that the monoclinic model only slightly differs from the tetragonal one previously obtained. The structure is made of continuous rows of FeO<sub>6</sub> faces sharing octahedra linked by PO<sub>4</sub> tetrahedra (see Fig. 3). In the monoclinic cell all these octahedra are aligned along the [111] and  $[\bar{1}\bar{1}\bar{1}]$  directions. Along these rows, two cations sites alternate with Fe—O distances slightly shorter for site 4(*c*) [on average Fec—O = 2.044 (4) Å] than for site 4(*b*) [on average Feb—O = 2.075 (4) Å]. However, one cannot attribute a specific charge to one site or to the other, because their coordinations are too similar and the average Fe—O distances are intermediate between those usually observed for Fe<sup>2+</sup> and Fe<sup>3+</sup> in an octahedral symmetry (2.14 and 2.01 Å). In fact, a calculation of the charges from the Fe—O distances with the bond valence model (Brown, 1992; Brese & O'Keeffe, 1991) gives 2.4<sup>+</sup> for Feb and 2.6<sup>+</sup> for Fec. This means that the two sites are carrying almost the same charge; this result is probably due to the significant

Table 3. Interatomic distances (Å) and angles (°) with standard deviations in parentheses

Feb—O1a	2.076 (8)	Feb—Fec	2.673 (1)
Feb—O1b	2.070 (6)	Fec—Feb	3.637 (1)
Feb—O2a	2.081 (6)	Feb—Feb	3.649 (1)
Fec—O1a	2.043 (6)	Fec—Fec	3.626 (1)
Fec—O1b	2.074 (7)	P—O1b	1.515 (8)
Fec—O2a	2.019 (5)	P—O1a	1.535 (7)
O1b—Feb—O2a	100.1 (2)	Feb—O2a—Feb	122.4 (5)
O1b—Feb—O1a	85.6 (3)	Fec—O2a—Feb	125.0 (2)
O1b—Feb—O2a	79.6 (2)	Fec—O2a—Feb	81.4 (1)
O2a—Fec—O1b	81.1 (4)	O1b—P—O1b	110.4 (6)
O1a—Fec—O1b	86.3 (3)	O1b—P—O1a	112.3 (4)
O2a—Fec—O1a	97.9 (2)	O1b—P—O1a	107.1 (3)
Fec—O2a—Fec	127.8 (6)	O1a—P—O1a	107.8 (6)

electronic exchange between the two cations at room temperature, as confirmed by a Mössbauer spectroscopy experiment (Malaman, Ijjaali, Ijjaali & Gleitzer, 1996). Then, even though the monoclinic deformation has been described, one cannot distribute the two cations on separate sites. A follow-up experiment was then performed on the evolution with temperature of this monoclinic deformation so as to elucidate the origin of the distortion.

#### 5. X-ray diffraction study above room temperature

This study has been carried out using conventional X-ray powder diffraction techniques (INEL CPW 120 diffractometer) with Co K $\alpha$  radiation. Several patterns were recorded in steps of 5 K, in the temperature range 300–500 K. In order to obtain a relative separation of the diffraction lines, we decided to explore the high-angle diffraction range and particularly the  $\theta = 33$ – $36^\circ$  angular domain. At room temperature (monoclinic cell) this angular range is characterized by the occurrence of two multiplets, labelled *A* and *B*, indexed as shown in

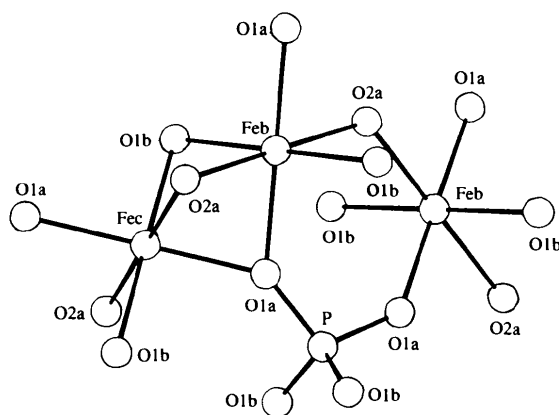
Fig. 3. View of the structure of  $\beta$ -Fe<sub>2</sub>PO<sub>5</sub>.

Fig. 4. Increasing temperature yields a slow narrowing of each multiplet and, at  $T = 420$  K, only two singlets are observed (Fig. 4), which correspond to the (224) and [(303)/(206)] lines of the previously published tetragonal cell.

The thermal evolution of the diffraction patterns clearly shows that the crystallographic transition (monoclinic  $\rightarrow$  tetragonal) occurs at  $T \simeq 415$  (5) K. Then, the monoclinic deformation, clearly visible at 300 K, only occurs at low temperature.

In a previous paper (Ijjaali *et al.*, 1990), we have shown that  $\beta$ -Fe<sub>2</sub>PO<sub>5</sub> is an antiferromagnet ( $T_N = 408$  K) characterized by ferromagnetic Fe<sup>2+</sup>/Fe<sup>3+</sup> couplings within the chains of face-sharing FeO<sub>6</sub> octahedra. Under these conditions, the structural transition observed around 415 K seems to be correlated to the magnetic ordering of the iron sublattice. The monoclinic distortion observed around  $T_N$  probably arises from a magnetostriction effect connected to the strong ferromagnetic interactions between iron atoms in each row of octahedra.

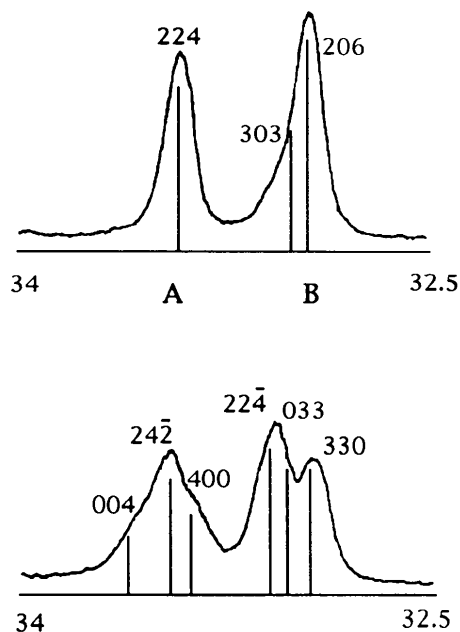


Fig. 4. Thermal evolution of the powder lines (224)<sub>i</sub> and [(303)<sub>i</sub>/(206)<sub>i</sub>].

## 6. Conclusions

This X-ray powder diffraction study provides new information on the structural behaviour of  $\beta$ -Fe<sub>2</sub>PO<sub>5</sub>. Synchrotron X-ray diffraction measurements clearly show that a monoclinic structure exists at room temperature. It corresponds to a slight deformation of the previously proposed tetragonal cell. Nevertheless, in the lower symmetry, the Fe—Fe distance within the rows of face-sharing octahedra remains remarkably short and the new structural arrangement cannot distinguish the Fe<sup>2+</sup> and Fe<sup>3+</sup> sites. This result is in agreement with the occurrence in this compound of a relatively fast Fe<sup>2+</sup>/Fe<sup>3+</sup> electronic exchange even at room temperature, as deduced from Mössbauer spectroscopy experiments.

On the other hand, our high-temperature X-ray diffraction studies show that a structural transition into the tetragonal symmetry occurs above 415 K. Under these conditions, the origin of this transition may be related to a strong magnetocrystalline effect at  $T_N$  (408 K).

In a forthcoming publication (Malaman, Ijjaali, Ijjaali & Gleitzer, 1996) conductivity measurement data and Mössbauer spectra will be presented and the electron transfer discussed in detail.

## References

- Berar, J. F. & Garnier, P. (1992). *APD 2nd Conference*. NIST (USA), Gaithersburg.
- Berar, J. F. & Lelann, P. (1991). *J. Appl. Cryst.* **24**, 1–5.
- Bessière, M., Bessenay, G., Frouin, J., Jouvin, M. & Lefebvre, S. (1987). *Nucl. Instrum. Methods A*, **261**, 591–597.
- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Brown, I. D. (1992). *Acta Cryst.* **B48**, 553–572.
- Ech-Chahed, B., Jeannot, F., Malaman, B. & Gleitzer, C. (1988). *J. Solid State Chem.* **74**, 47–59.
- Elkaïm, E., Lefebvre, S., Kahn, R., Berar, J. F., Lemonnier, M. & Bessière, M. (1992). *Rev. Sci. Instrum.* **63**(1), 988–991.
- Ijjaali, M., Malaman, B., Gleitzer, C., Warner, J. K., Hriljac, J. A. & Cheetham, A. K. (1990). *J. Solid State Chem.* **86**, 195–205.
- Malaman, B., Ijjaali, M., Ijjaali, I. & Gleitzer, C. (1996). *Hyperfine Interactions*. To be published.
- Modaressi, A., Courtois, A., Gerardin, R., Malaman, B. & Gleitzer, C. (1981). *J. Solid State Chem.* **40**, 301–311.
- Warner, J. K., Cheetham, A. K., Cox, D. E. & Von Dreele, R. B. (1992). *J. Am. Chem. Soc.* **114**, 6074–6080.