LiFeP$_2$O$_7$: Structure and Magnetic properties

D. Riou, N. Nguyen, R. Benloucif and B. Raveau.

Laboratoire CRISMAT-ISMRa 14050 CAEN Cedex - FRANCE

ABSTRACT :

In order to compare the structural and magnetic properties of the diphosphates AFeP$_2$O$_7$ (A=Li, Na, K), the structure of the LiFeP$_2$O$_7$ compound was redetermined and the magnetic measurements of the lithium, sodium and potassium phases were performed. It is shown that LiFeP$_2$O$_7$ does not exhibit any abnormal O-O distances contrary to the results obtained by previous authors. A new description of the structure is proposed. The three compounds exhibit an antiferromagnetic transition at $T_N \approx 20$ K confirming the results obtained by Hagenmüller et al (6). The paramagnetic temperature θ_p exhibits a regular evolution which can be explained on the basis of Fe-Fe distances and of the number of nearest Fe^{3+} ions surrounding one iron cation.

MATERIALS INDEX : sodium, lithium, potassium, iron, oxide, phosphate.

Former investigations of the AFe^{III}P$_2$O$_7$ (A=Li, Na, K) diphosphates series have shown the existence of three structural types (1,2,3) all characterized by a mixed framework of corner-sharing FeO$_6$ octahedra and P$_2$O$_7$ units whose distribution defines different sorts of tunnels. In the three structures, octahedral layers alternate with tetrahedral layers, the difference between them resulting principally from the conformation of the diphosphate groups. Among these oxides, the lithium phosphate LiFeP$_2$O$_7$ presents, according to Genkina et al. (1), some abnormal O-O distances ranging from 2.05 Å to 3.05 Å in the same octahedron. Moreover, the study of the magnetic properties of NaFeP$_2$O$_7$ by Hagenmüller et al. (6) has shown the existence of antiferromagnetic ordering with a weak ferromagnetic component below 30 K. The present paper deals with the redetermination of the structure of LiFeP$_2$O$_7$ and with the magnetic properties of the diphosphates LiFeP$_2$O$_7$ and KFeP$_2$O$_7$.

EXPERIMENTAL :

The diphosphates $AFe^{III}P_2O_7$ were synthesized from pulverized mixtures of A_2CO_3 (A=Li, Na, K), Fe_2O_3 and $(NH_4)_2\, HPO_4$ in ratios 1 : 1 : 4. The powders used for the magnetic measurements were heated in air in platinum crucible at 973 K for $LiFeP_2O_7$ and $KFeP_2O_7$ and 1073 K for $NaFeP_2O_7$ several days. For the growth of $LiFeP_2O_7$ crystals, the mixture was first heated in air at 893 K to decompose the phosphate and carbonate, then the resultant product was ground and heated at 1423 K for two days in an evacuated sealed silica ampoule. After cooling at the rate of 2 K/h down to 1133 K and quenching at room temperature, a fragment with indefinite facies of 48 x 96 x 192 mm dimensions was choosen for the crystallographic study.

Table 1 : Summary of crystal data, intensity measurements
and structure refinement parameters for $LiFeP_2O_7$.

1- Crystal data

Space group	$P2_1$
cell dimensions	a=4.8229 (2) Å
	b=8.0813 (5) Å β=109.387 (5)°
	c=6.9419 (6) Å
Volume	V=255.22 (4) Å^3
Z	2

2- Intensity measurement

λ (Mo Kα)	0.71073 Å
scan mode	ω - 4/3 θ
scan width (°)	0.90 + 0.35 tan θ
slit aperture (mm)	1 + tan θ
standard reflections	9 0 0,0 16 0 and 0 0 13 measured every 4000 s (no decay)
reflections with $I \geq 3\sigma$	1957
μ_l (cm^{-1})	36.26

3- Structure solution and refinement

Parameters refined	100
agreement factors	R=0.028, R_W=0.035
weighting scheme	W=1
Δ/σ_{max}	0.01

The cell parameters (Table 1) were determined and refined by diffractometric study at 294 K with a least-squares refinement based upon 25 reflections with $18 \leq \theta \leq 22°$.

The data were collected on a CAD4 Enraf-Nonius diffractometer (data collection parameters in Table 1). The reflections were corrected for Lorentz and polarisation effects ; no absorption corrections were performed.

The structure was solved by direct methods using the MULTAN program (4). Refinement of the atomic coordinates and their anisotropic thermal parameters led to R=0.028 and Rw=0.035. Atomic parameters are given in Table 2. [List of structure factors and anisotropic thermal motion parameters are available on request to the authors].

The magnetic susceptibility was measured versus temperature from 4 to 700 K with a Faraday balance.

Atom	x	y	z	B_{eq} (Å^2)
Li	0.803(2)	0.384(1)	0.819(1)	2.0(1)
Fe	0.21948(7)	0.250	0.23398(5)	0.387(3)
P(1)	0.7939(1)	0.47040(9)	0.41665(9)	0.406(7)
P(2)	0.6008(1)	0.07093(9)	0.98019(9)	0.368(7)
O(1)	0.4029(4)	0.0722(3)	0.1099(3)	0.68(2)
O(2)	0.8141(4)	0.2156(2)	0.0198(3)	0.61(2)
O(3)	0.1318(4)	0.0616(3)	0.3813(3)	0.70(2)
O(4)	0.0619(4)	0.4302(3)	0.3611(3)	0.84(3)
O(5)	0.2481(4)	0.4056(2)	0.0103(3)	0.58(2)
O(6)	0.3985(4)	0.1016(3)	0.7475(3)	0.73(3)
O(7)	0.6082(4)	0.3197(3)	0.4183(3)	0.78(3)

Table 2 : Atomic parameters

$$B_{eq} = 4/3 \ (\beta_{11}.a^2 + \beta_{22}.b^2 + \beta_{33}.c^2 + \beta_{12} \ a.b.\cos\gamma + \beta_{13} \ a.c.\cos\beta + \beta_{23} \ b.c.\cos\alpha)$$

DESCRIPTION OF THE STRUCTURE OF LiFeP$_2$O$_7$

The structure of LiFeP$_2$O$_7$ (Fig.1) is characterized by the arrangement of FeO$_6$ octahedra and diphosphate groups previously described by Genkina et al. (1). Each octahedron is linked to six PO$_4$ tetrahedra belonging to five different phosphate groups ; each FeO$_6$ octahedron shares two corners with the same P$_2$O$_7$ group, forming a [FeP$_2$O$_{11}$] unit already encountered in many diphosphates (2, 3, 5).
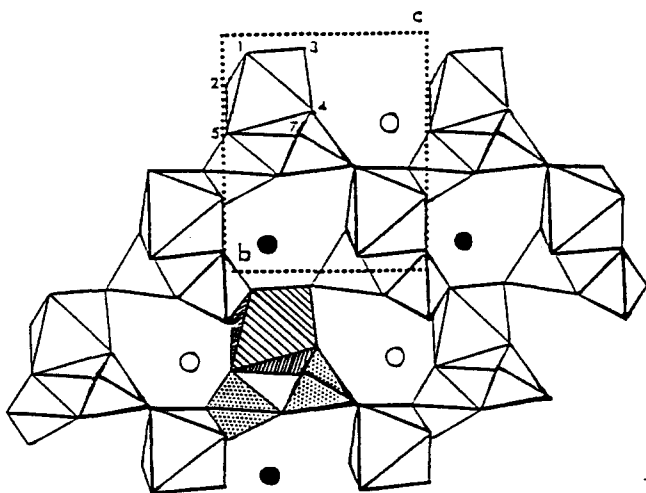

Figure 1 : Projection of the structure of LiFeP$_2$O$_7$ onto (100).

Figure 2 : Columns of corner-sharing [FeP$_2$O$_{11}$] units running along $\vec{a}$.
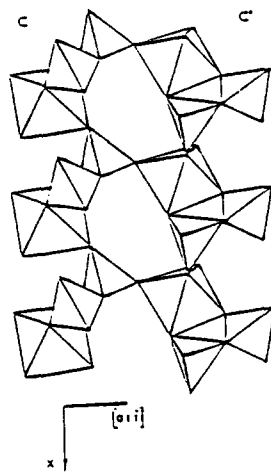
Nevertheless, these results differ from those obtained by Genkina et al. (1) by the O-O distances which are absolutely normal (Tables 3-4). One does not observe O-O distances as long as

2.05 Å in the FeO_6 octahedra contrary to these authors but distances ranging from 2.614 (3) to 4.000 (3) Å. Consequently, the FeO_6 octahedra are almost regular (Table 3) with homogeneous Fe-O bond lengths ranging from 1.957 (7) to 2.04 (1) Å. In the same way, the O-O distances in the PO_4 tetrahedra are those usually observed ranging from 2.434 (3) to 2.547 (4) Å. The P-O distances are characteristic of diphosphate groups, i.e. one observes one long P-O distance with the bridging oxygen O (6) of P_2O_7 and three shorter P-O bonds with terminal oxygen atoms linked to Fe (Table 4). The diphosphate group exhibits an almost eclipsed conformation with a P-O-P angle of 128.8° (2) intermediate between the values observed for $KFeP_2O_7$ and $NaFeP_2O_7$ (124.3(1)° and 132.86(9)° respectively).

Table 3 :Distances (Å) and angles (°) in the P_2O_7 groups.

P (1)	O (3^{iv})	O (4^{ii})	O (6^{iv})	O (7)
O (3^{iv})	1.519 (3)	2.511 (3)	2.460 (4)	2.484 (4)
O (4^{ii})	112.5 (2)	1.502 (3)	2.511 (4)	2.514 (4)
O (6^{iv})	103.8 (2)	107.7 (2)	1.607 (3)	2.548 (4)
O (7)	110.0 (2)	112.9 (2)	109.4 (1)	1.514 (3)

P (2)	O (1^{iii})	O (2^{iii})	O (5^{v})	O (6)
O (1^{iii})	1.514 (3)	2.547 (4)	2.505 (3)	2.520 (4)
O (2^{iii})	114.1 (2)	1.521 (3)	2.524 (4)	2.434 (3)
O (5^{v})	111.7 (2)	112.6 (1)	1.513 (3)	2.518 (4)
O (6)	107.8 (1)	102.2 (1)	107.7 (1)	1.605 (3)

The diagonal terms are the P-O distances, the terms above the diagonal are the O-O distances and below are the O-P-O angles.

Table 4 : Distances (Å) and angles (°) in the FeO_6 octahedra

Fe	O (1)	O (2^i)	O (3)	O (4)	O (5)	O (7)
O (1)	2.023 (8)	2.936 (4)	2.627 (4)	3.488 (4)	2.819 (4)	2.856 (4)
O (2^i)	92.4 (4)	2.04 (1)	2.764 (4)	2.858 (4)	2.614 (3)	4.000 (3)
O (3)	82.6 (1)	87.4 (4)	1.957 (7)	2.996 (4)	3.954 (4)	3.050 (4)
O (4)	176.8 (6)	90.5 (5)	99.1 (5)	1.981 (8)	2.869 (4)	2.684 (4)
O (5)	87.9 (4)	79.6 (4)	163.6 (6)	91.1 (2)	2.038 (9)	2.874 (4)
O (7)	91.3 (5)	170.4 (3)	101.9 (5)	85.6 (3)	91.6 (4)	1.97 (1)

The diagonal terms are the Fe-O distances, the terms above the diagonal are the O-O distances and below are the O-Fe-O angles.

An original description of the structure deals with the stacking of the $[FeP_2O_{11}]$ units. The latters share the corners of their polyhedra forming infinite chains $[FeP_2O_{11}]_\infty$ running along $\vec{a}$ (Fig.2). Laterally, such an infinite chain C shares the corners of its polyhedra with four other similar chains C' which are symmetrically equivalent to C by the 2_1 screw axis. Thus, the $[FeP_2O_7]_\infty$ framework can be described from the single stacking of parallel $[FeP_2O_{11}]_\infty$ chains sharing the corners of their polyhedra. The connection between these chains defines tunnels running along $\vec{a}$. These tunnels are delimited by four columns (two C + two C') and present an heptagonal window (Fig.1). Each tunnel shows perpendicularly to the [011], [0$\bar{1}$1], [01$\bar{1}$] and [0$\bar{1}$1] directions lateral windows with hexagonal section (Fig.2) permitting communication between tunnels. A geometrical study of the host-lattice of $LiFeP_2O_7$ shows that a displacement of the Li^+ ions along the axis of the tunnels and through the lateral windows is possible. This suggests a

possibility of ionic conductivity for this compound. In fact, the Li^+ ions are located in off-centred positions inside the tunnels (Fig.1) where they realize a fourfold pseudo-tetrahedral coordination (Table 5), a fifth neighfour lying at 2.674 (3) Å.

The structure of $K_{0.17}MoP_2O_7$ (5) is also characterized by parallel columns of $[MoP_2O_{11}]$ units delimiting tunnels, but the mode of connection of the $[MoP_2O_{11}]$ units in a chain differs from that of $LiFeP_2O_7$. Moreover, it is worth pointing out that the framework of $LiFeP_2O_7$ presents layers of FeO_6 octahedra alternating with layers of P_2O_7 groups (Fig.3), feature which also appears in $KFeP_2O_7$ and $NaFeP_2O_7$.
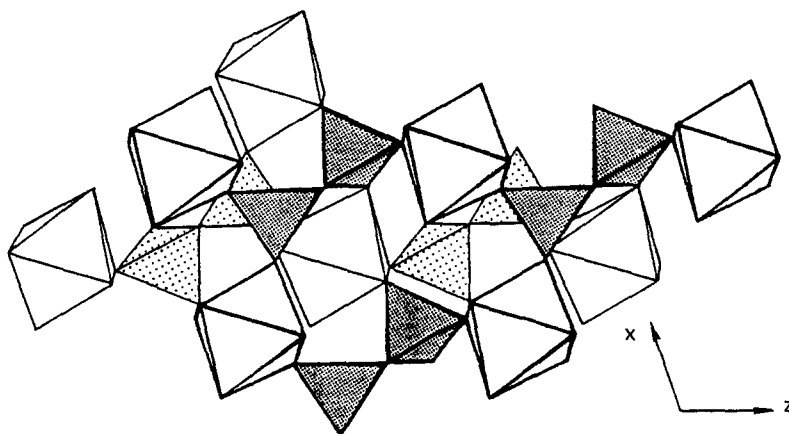

Figure 3 : Projection of the structure of $LiFeP_2O_7$ onto (010) showing the octahedral layers which alternate with the tetrahedral layers.

Table 5 : Distances Li-O (en Å)

Li-O (1^{iv})	1.969 (3)
Li-O (2^{iii})	1.936 (3)
Li-O (3^{iv})	2.093 (3)
Li-O (5^{vi})	2.123 (3)

Symmetry codes :

i :	x - 1	y	z
ii :	1 + x	y	z
iii :	x	y	1 + z
iv :	1 - x	1/2 + y	1 - z
v :	1 - x	y - 1/2	1 - z
vi :	1 + x	y	1 + z

MAGNETIC MEASUREMENTS

The variation of the reciprocal molar susceptbility χ_M^{-1} versus temperature shows that the three compounds $AFeP_2O_7$ (A=Li, Na, K) exhibit an antiferromagnetic transition at $T_N \approx 20$ K (Fig.4). The paramagnetic temperature θ_P, the Néel temperature and the number of Bohr magnetons

n_β calculated from the curves χ_M^{-1} = f (T) in the temperature range 100-700 K of these phases are given in table 6. The results observed by Hagenmüller et al. (6) for $NaFeP_2O_7$ are confirmed. The n_β values are in agreement with the theoritical value of Fe^{3+} in high spin configuration (5.9 μ_B).
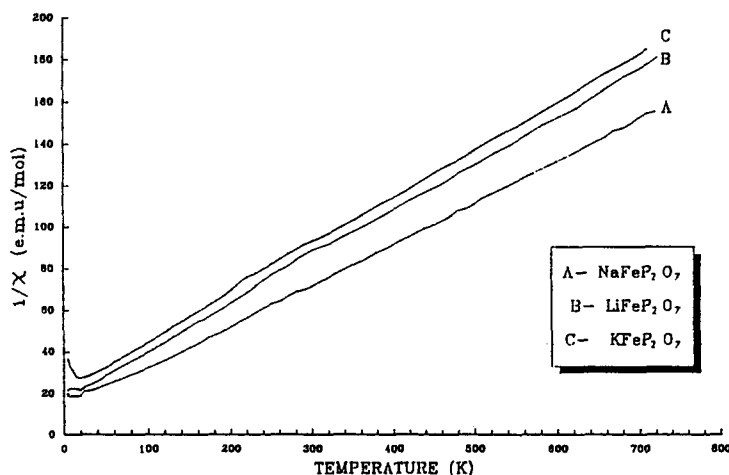

Figure 4 : Reciprocal molar magnetic susceptibility vs temperature of $AFeP_2O_7$ compounds.

Compound	Fe^{3+} neighbouring	mean distance Fe-Fe (Å)	n_β (μ_B)	T_N (K)	θ_P (K)
$KFeP_2O_7$	8	5.641	5.93	20 ± 5	-90 ± 5
$LiFeP_2O_7$	10	5.632	5.89	22 ± 5	-73 ± 5
$NaFeP_2O_7$	10	5.615	6.20	22 ± 5	-58 ± 5

Table 6 : Magnetic characteristics of the $LiFeP_2O_7$, $NaFeP_2O_7$ and $KFeP_2O_7$ compounds.

       One observes a decrease of magnetic susceptibility, i.e. the paramagnetic temperature θ_P from sodium to potassium compounds via lithium phase. This fact is in agreement with the structural results : the mean interatomic distances Fe-Fe of FeO_6 octahedra (Table 6) increase from $NaFeP_2O_7$ to $KFeP_2O_7$ via $LiFeP_2O_7$ while the number of first neighbours Fe^{3+} ions surrounding every Fe^{3+} ion decrease. These two features suggest that the magnetic interactions between Fe^{3+} ions in $NaFeP_2O_7$ are stronger than these of the two other phases.

CONCLUDING REMARKS :

       These results demonstrate that there is no anomaly in the structure of $LiFeP_2O_7$, which exhibits usual interatomic distances. A new description of the structure can be proposed which consists of corner-sharing $[FeP_2O_{11}]_\infty$ chains forming a tunnel structure where the Li^+ ions are located. The size of these cations compared to those of the windows boarding the tunnels suggest

the possibility of ionic conductivity. The magnetic characteristics confirm the antiferromagnetic transition previously established by Hagenmüller et al. (6) with a Neel temperature close to 20 K.

The evolution of θ_p observed is normal if one takes into account the fact that the paramagnetic temperature decreases as the number of nearest Fe^{3+} neighbours for one Fe^{3+} cation decreases and as the Fe-Fe distance increases.

REFERENCES

1 : E.A. Genkina, B.A. Maksimov, V.A. Timofeeva, A.B. Bykov and O.K. Mel'Nikov,
Dokl. Akad. Nauk SSSR 284, 864-867 (October 1985)
2 : M. Gabelica-Robert, M. Goreaud, Ph. Labbe and B. Raveau,
J. of Solid State Chem. 45, 389-395 (1982)
3 : D. Riou, Ph. Labbe and M. Goreaud, Eur. J. Sol. St. Inorg. Chem. 25, 215-229 (1988)
4 : P. Main and Coll., Department of physics, University of York, England, July 1982
5 : A. Leclaire, M.M. Borel, A. Grandin and B. Raveau
J. of Solid State Chem. 78, 220-226 (1989)
6 : T. Moya-Pizarro, R. Salmon, L. Fournes, G. Leflem, B. Wanklyn and P. Hagenmuller,
J. of Solid State Chem. 53, 387-397 (1984)