Nuclear and magnetic structures of the two-dimensional antiferromagnet $KFeF_4$

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Abstract.   The nuclear and magnetic structures of the layered compound KFeF$_4$ (that undergoes structural and magnetic phase transitions at $T_c = 380$ K and $T_N = 137$ K respectively) are investigated by neutron powder diffraction over a large temperature range (673–2 K). At 673, 543 and 413 K, it is deduced that KFeF$_4$ exhibits the ideal high symmetry structure (aristotype) with *Bmmb* space group; there is no evidence for the phase transition observed by Hidaka *et al* at 563 K. The diffraction patterns collected below T_c (at 300, 170 K) are consistent with the *Pcmn* space group and the phase transition mainly arises from FeF$_6$ octahedron rotation around the [001] axis. The magnetic structure is reinvestigated in the framework of the new low temperature space group. It is deduced that the moments are aligned normally to the FeF$_6$ sheets with antiferromagnetic coupling in the planes. It seems that only the coexistence of two phases can describe the magnetic interactions between the planes.

1. Introduction

The tetrafluoroaluminates AA1F$_4$ with T1A1F$_4$ type structure have been shown to undergo various structural phase transitions (SPTs), i.e. displacive SPT (RbA1F$_4$, T1A1F$_4$), order–disorder SPT (NH$_4$A1F$_4$) and martensitic SPT (KA1F$_4$) arising from gliding of A1F$_6$ octahedra sheets (Launay *et al* 1985). This latter case is of special interest since, unlike most of the metallic alloys (where such a kind of transition is encountered), the martensitic phase transition of KA1F$_4$ (that occurs at about 260 K) has been unambiguously shown to be related to the softening of a (flat) phonon branch of the high temperature phase. This led to the proposition of a model describing the mechanism of the transition (Bulou *et al* 1989). Going farther in the description of such a transition requires investigation of the lattice dynamics properties of the low temperature phase on single crystals. However, the single crystals (which are grown in the high temperature phase) irreversibly break at the transition. So a system having the same structure as the KA1F$_4$ low temperature phase could be useful for such an analysis. KFeF$_4$ is one of these systems (Heger *et al* 1971). Moreover KFeF$_4$ is of special interest in itself. According to Hidaka *et al* (1979) it undergoes several structural phase transitions at $T = 563$ K and $T' = 368$ K and the sequence of space groups *Ammm*, *Amma* and *Pmmn* was proposed. On the basis of these results, Saint-Grégoire *et al* (1985) predicted that an incommensurate phase might exist in the vicinity of T'. After this Lapasset *et al* (1986) investigated the structures by x-ray diffraction at 415 and 295 K and they proposed the *Amma* and *Pcmn* symmetries respectively.

An additional structural investigation by Sciau and Grebille (1989), who considered phase III as a modulated structure of the average of phase II, has confirmed the results of Lapasset *et al* (1986) and similar atomic coordinates were obtained. The present work concerns the structural investigation as a function of temperature, in a large temperature range, in order to demonstrate the atomic displacements that drive the transitions. The temperature range above and below $T = 563$ K was the object of special attention in order to check the existence of the phase transition described by Hidaka from x-ray diffraction.

KFeF$_4$ is also interesting for its magnetic properties. Heger *et al* (1971) who first described its structure discovered an antiferromagnetic phase transition at $T_N = 137$ K. On the basis of the *Amma* nuclear symmetry a magnetic structure with both 'ferromagnetic and antiferromagnetic coupling' between second nearest FeF$_6$ sheets was proposed. It is now known that, in the temperature range when the magnetic ordering occurs, the nuclear structure is indeed *Pcmn* and a reinvestigation of the magnetic structure is necessary. Such a reinvestigation is also dictated by the fact that KFeF$_4$ belongs to a very rare kind of magnetic ion network 'intermediate' between the RbFeF$_4$ and Rb$_2$MnF$_4$ ones.

2. Experiment

The growth of an KFeF$_4$ single crystal often shows inclusions of black K$_x$FeF$_3$ and green K$_2$FeF$_5$. So, in order to have pure KFeF$_4$ powder, the sample was obtained from the grinding of pure single crystals prepared at the Laboratoire de Physique de l'Etat Condensé by the horizontal Bridgman method at $T = 933$ K in a platinum crucible. The powder was composed of aggregates of inhomogeneous size which were not squeezed together to avoid preferred orientation.

The neutron diffraction experiments were performed at the I.L.L. on the powder diffractometers D1A at $\lambda = 1.909$ Å and D1B at $\lambda = 2.58$ Å. The samples were placed in cylindrical vanadium cans (diameter: 12 mm) held in a furnace (equipped with a vanadium heating element and operating under secondary vacuum) or in a standard helium cryostat. The high resolution of D1A at large angle was used to obtain extensive and accurate data for the nuclear structures of KFeF$_4$ at 673, 413, 300, 170, 135 and 5 K over a large angular range ($6° \leqslant 2\vartheta \leqslant 160°$) in steps of $0.05°$. A preliminary neutron diffraction powder pattern was collected at $\lambda = 2.98$ Å in order to check the lattice symmetry at room temperature. The high flux and good resolution of D1B at low angle was used to study the magnetic structure at $T = 2$ K.

The D1A and D1B patterns were analysed by the Rietveld profile method (Rietveld 1969) modified by Hewat (1973). The nuclear scattering lengths $b(10^{-12}$ cm$)$ were taken from Koester and Rauch (1981) and the magnetic form factors of Fe^{3+} ions from Watson and Freeman (1961). Note that, in spite of a careful preparation of the powder, the refinements of the patterns required us to include a preferred orientation parameter with a significant value.

3. Nuclear structure

In order to establish connections between the KFeF$_4$ symmetry and the T1A1F$_4$ type symmetry, the crystallographic axis will be chosen such that a and b are set in the FeF$_6$ sheet and c perpendicular to this plane. So the space group of the high symmetry phase is *Bmmb* instead of *Amma*. The different structures of KFeF$_4$ will be established according to an ideal orthorhombic one represented in figure 1(a) (the so called archetype or aristotype)
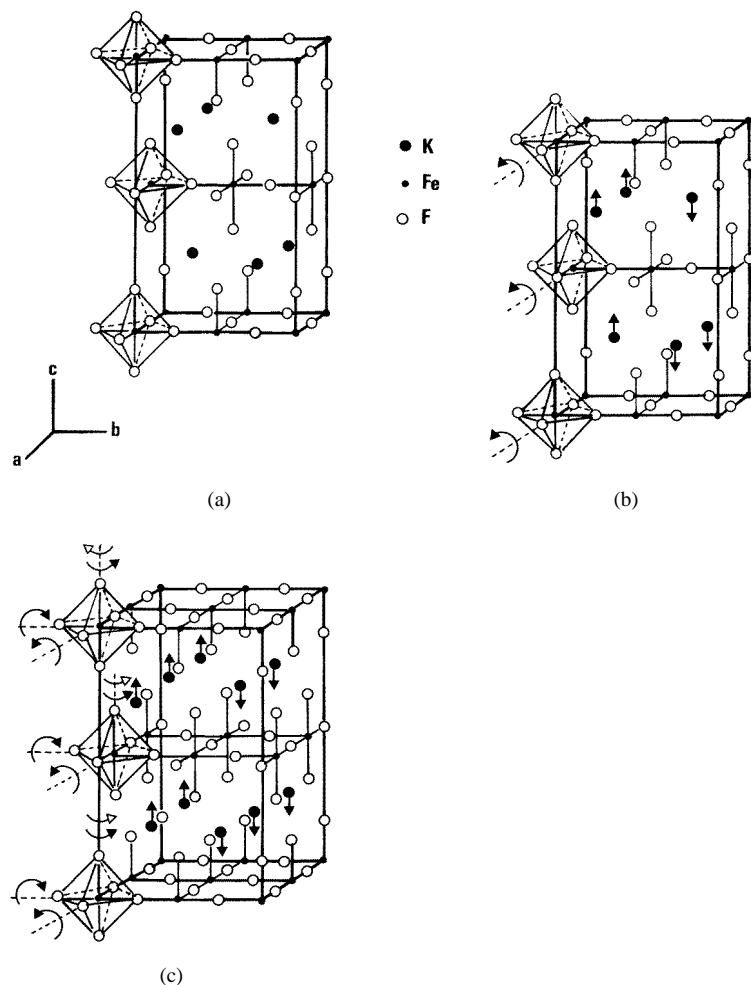
Figure 1. (a) Ideal structure of KFeF$_4$. (b) Phase I of KFeF$_4$. (c) Phase II of KFeF$_4$. The FeF$_6$ tilts and K displacements are indicated by arrows: full triangles for KFeF$_4$; open triangles for KAlF$_4$.

and corresponding to the *Bmmb* space group where (i) the octahedra tilts around the crystallographic axis are equal to zero, (ii) the potassium ions coordinates along the *c* axis are 1/4 and 3/4.

3.1. The high temperature phase

Figure 2 shows the diffraction patterns at 673 K (a) and 413 K (b). It is clear from a careful study that these two patterns are similar and so there is no evidence for the 563 K phase transition described by Hidaka *et al* (1979). Note in particular that the 038 line, that should have vanished above 563 K according to Hidaka, still is observed at 673 K (figure 2). Such a conclusion is also supported by the refinement since the 673 and 413 K patterns can be described by the *Bmmb* space group and similar *R* factors are obtained. The results of the refinements at 413 K are summarized in table 1. For comparison the parameters and
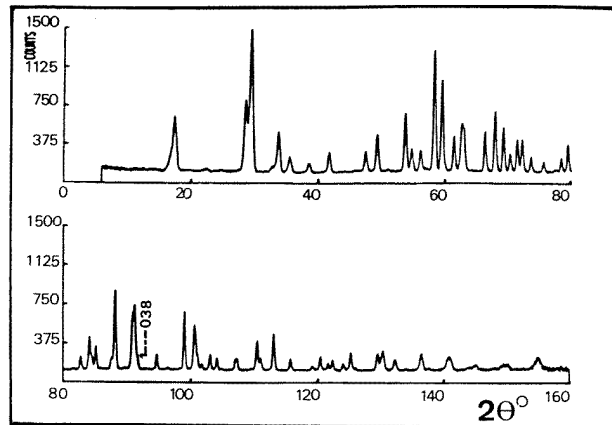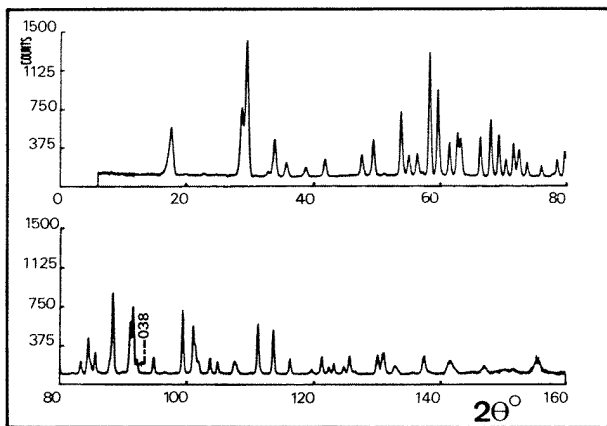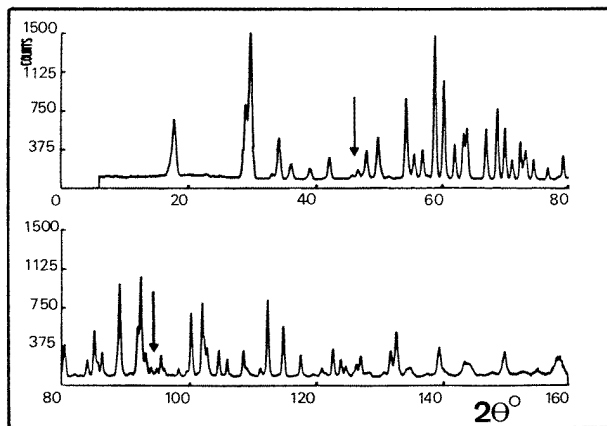
Figure 2. Neutron powder diffraction patterns of $KFeF_4$ at 673 K (a), 413 K (b) and 300 K (c) with $\lambda = 1.916$ Å (D1A). The 038 line that should vanish above 563 K (Hidaka *et al* 1979) is indicated. Arrows in (c) show some diffraction lines that grow in phase III.

Table 1. Results of the refinements in the *Bmmb* symmetry at 413 K: our work; 415 K: Lapasset *et al* (1986).

T (K)	R_{nuc}	R_{prof}	a_I(Å)	b_I (Å)	c_I (Å)	
413	10.65	14.52	3.9153(1)	7.6621(3)	12.3512(5)	
415 K			3.92(1)	7.68(1)	12.39(2)	

	Site	x	y	z	B_{iso} (Å^2)
Fe	4a	0	0	0	1.22(6)
					0.87(1)
K	4c	0	0.25	0.728 1(5)	2.5(2)
				0.728 52(9)	2.16(3)
F$_1$	4b	0	0	0.5	3.3(1)
					3.20(8)
F$_2$	4c	0	0.25	0.9656(4)	2.5(1)
				0.9659(3)	2.45(7)
F$_3$	8f	0	0.0485(4)	0.1495(3)	2.1(1)
			0.0463(3)	0.1488(2)	2.03(4)

positions obtained by the x-ray diffraction study performed by Lapasset *et al* (1986) at 415 K are recalled in this table.

These results show that the phase I of KFeF$_4$ (figure 1(b)) is derived from the ideal structure by octahedra tilts around [100] (about 11 degrees) and K$^+$ displacements along [001]. It must be noted that both displacements are consistent with the *Bmmb* symmetry.

3.2. The low temperature phase

At 300 and 170 K some weak intensity lines are observed in addition to the high temperature phase ones and they can be unambiguously attributed to a doubling of the *a* parameter. These lines are denoted by arrows in figure 2(c). Among the possible *k* subgroups of *Bmmb* (table 2) the systematic extinctions lead us to choose the *Pcmn* space group (the *Pmmn* group can be ruled out by the fact that all the 0*kl* lines observed present the limiting condition l = 2*n*). This result is consistent with previous studies by Lapasset *et al* (1986). Parameters and refinement in the *Pcmn* group are reported in table 3 together with their corresponding values obtained by Lapasset *et al* (1986).

With respect to phase I, phase II of KFeF$_4$ (figure 1(c)) mainly differs by:

- octahedra tilts around [001] (about 8 degrees)
- small octahedra tilts around [010] (about 2 degrees).

These two tilts are responsible for the doubling of the *a* parameter.

Note that attempts to refine the low temperature patterns with the same space group as KA1F$_4$($P2_1/m$) failed. In fact the pattern collected at $\lambda = 2.98$ Å does not exhibit any lines inconsistent with the orthorhombic symmetry such as occurs in KA1F$_4$ (Launay 1984).

All these neutron powder diffraction results are consistent with the x-ray diffraction studies of Lapasset *et al* (1986) and those of Sciau and Grebille (1989).

Table 2. k subgroups of *Bmmb*.

| Sub-group	Cond. limiting possible reflections	Lines observed
Pmmb	$hk0 : k = 2n$	310, 130, 150, 510, ...
	$0k0 : (k = 2n)$	
Pmab	$hk0 : k = 2n$	310, 130, ...
	$h01 : h = 2n$	103, 104, 105, ...
	$0k0 : (k = 2n)$	
	$h00 : (h = 2n)$	
Pmmn	$hk0 : h + k = 2n$	
	$h00 : (h = 2n)$	
	$0k0 : (k = 2n)$	
Pman	$hk0 : h + k = 2n$	
	$h01 : h = 2n$	306, ...
	$h00 : (h = 2n)$	
	$0k0 : (k = 2n)$	
Pcmn	$hk0 : h + k = 2n$	
	$0k1 : 1 = 2n$	
	$h00 : (h = 2n)$	
	$0k0 : (k = 2n)$	
	$001 : (1 = 2n)$	
Pcab	$0k1 : 1 = 2n$	
	$hk0 : k = 2n$	310, 130, ...
	$h01 : h = 2n$	306, ...
	$h00 : (h = 2n)$	
	$0k0 : (k = 2n)$	
	$001 : (1 = 2n)$	
Pcan	$h01 : h = 2n$	306, ...
	$0k1 : 1 = 2n$	
	$hk0 : k + k = 2n$	

3.3. Discussion and analysis of results

The reliability of the structural parameter can be checked from the values of some typical interionic distances. Figure 3 shows that the FeF interionic distances are roughly temperature independent and are close to the expected one (1.98 Å) (Shannon 1976). Moreover, even at very low temperature (low symmetry phase) the octahedron distorsion represented in figure 4 is small in the (a, b) plane (the more important distortion occurs in the (b, c) plane which is the plane where the octahedron tilts are the largest). So the temperature behaviour of the lattice parameters can be mainly imputed to the rotation of rigid octahedra. For instance the large octahedron rotation angle around the [100] axis explains the fact that the b parameter (figure 5) is smaller than the a parameter. The transition at T_{c_1} can be mainly described in terms of octahedron rotation around the [001] axis. It must be noted that in phase II the octahedron tilt is always very large (7.3° at 300 K).

It can be noted that, although the low temperature phases of KFeF$_4$ and KAlF$_4$ belong to the same structural type, the space groups are different. The difference can be readily described in terms of octahedron tilts (figure 1(c)): the octahedra belonging to second

Table 3. Parameters and results of refinements in *Pcmn* at 300 K (present work) and 295 K (Lapasset *et al* 1986).

T (K)	R_{nuc}	R_{prof}	a_{II} (Å)	b_{II} (Å)	c_{II} (Å)
300	11.57	13.71	7.7998(2)	7.6317(2)	12.3294(3)
295 K			7.81(1)	7.64(1)	12.33(2)

	Site	x	y	z	B_{iso} (Å^2)
Fe	8d	0.1266(5)	0.0003(3)	0.2498(4)	0.76(3)
		0.1255(1)	0.00035(5)	0.24894(4)	0.606(3)
K$_1$	4c	0.123(2)	0.25	0.974(1)	1.57(8)
		0.1210(3)		0.97551(8)	1.46(2)
K$_2$	4c	0.120(2)	0.75	0.513(1)	1.57(8)
		0.1201(3)		0.51705(7)	1.34(2)
F$_1$	8d	0.1243(9)	0.0320(4)	0.7543(5)	2.01(6)
		0.1227(5)	0.0313(2)	0.7517(2)	1.75(3)
F$_{21}$	4c	0.0952(7)	0.25	0.2147(7)	0.98(6)
		0.0959(5)		0.2145(3)	1.26(6)
F$_{22}$	4c	0.1592(7)	0.75	0.2822(8)	0.98(6)
		0.1540(5)		0.2827(3)	1.36(7)
F$_{31}$	8d	0.1328(8)	0.0489(7)	0.4016(5)	1.47(4)
		0.1202(6)	0.0476(3)	0.3983(2)	1.36(4)
F$_{32}$	8d	0.1372(7)	0.9510(8)	0.1004(4)	1.47(4)
		0.1308(6)	0.9543(3)	0.0997(2)	1.41(4)
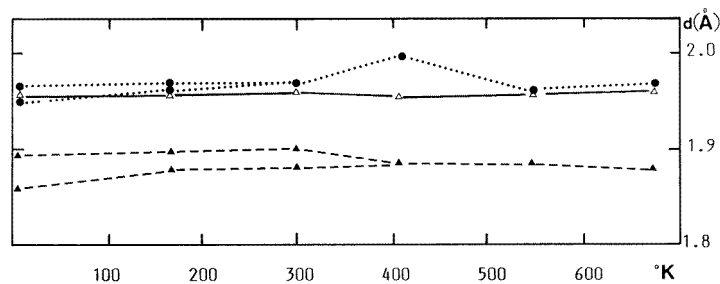
Figure 3. Interionic Fe–F distances as a function of temperature (circle: Fe–F$_2$, open triangle: Fe–F$_1$, full triangle: Fe–F$_3$).

neighbour sheets rotate in the same sense in KFeF$_4$ and in the opposite sense in KA1F$_4$. Actually the KFeF$_4$ symmetry is also encountered in KTiF$_4$ (Sabatier *et al* 1979), KVF$_4$ (Babel 1968) and KGaF$_4$ (Courbion 1979) while the KA1F$_4$ one has never been encountered elsewhere.

Finally, an important result is that, from the present work, there is no signature for the phase transition observed at 563 K by Hidaka *et al* (1979). Let us first notice that, if present, this transition should have been reconstructive: *Bmmb* being the highest symmetry for the KFeF$_4$ structural arrangement, a phase transition to the *Bmmm* space group† would have required a gliding of the potassiums along [100] of half the *a* parameter (of the ideal
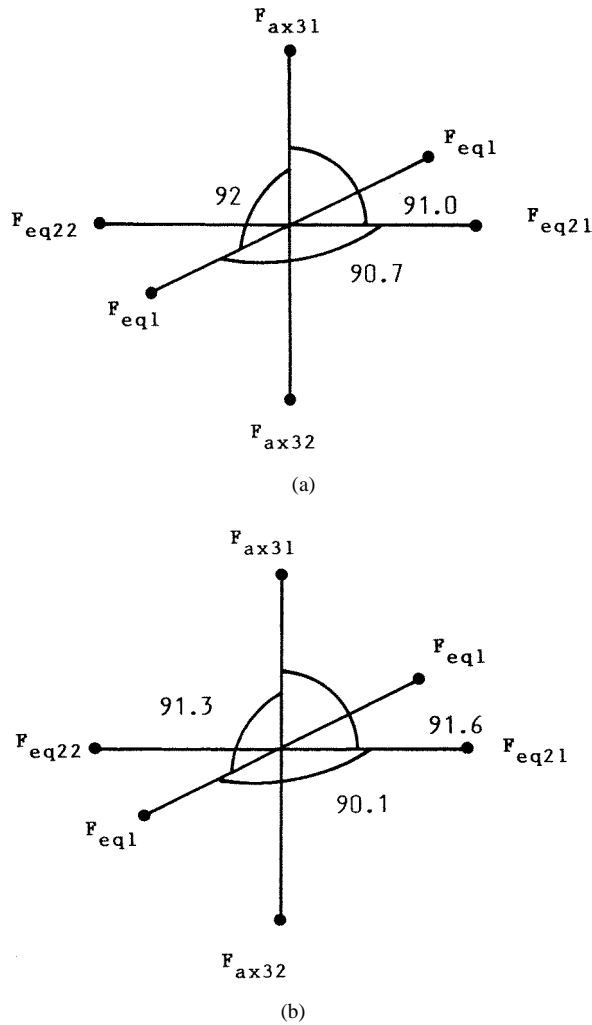
† *Ammm* with Hidaka's conventions.

Figure 4. Bond angles in FeF$_6$ octahedra of KFeF$_4$ at 300 K (a) and 5 K (b).

structure). On the other hand the existence of a phase transition at 563 K was deduced from two different observations: an anomaly of the dielectric permittivity and the vanishing of the 038 diffraction line; from the present study, this line still is observed at 673 K (and the calculated value is significant) and so it can be thought that the signal that vanished at 563 K was not a diffraction line. Its origin together with the origin of the dielectric anomalies that occur at 563 K remains to be explained.

4. Magnetic structure of KFeF$_4$ at 2 K

Previous susceptibility measurements on powder of KFeF$_4$ have shown that dominant antiferromagnetic interactions are established below $T_N = 137$ K (Heger *et al* 1971, Heger and Geller 1972).
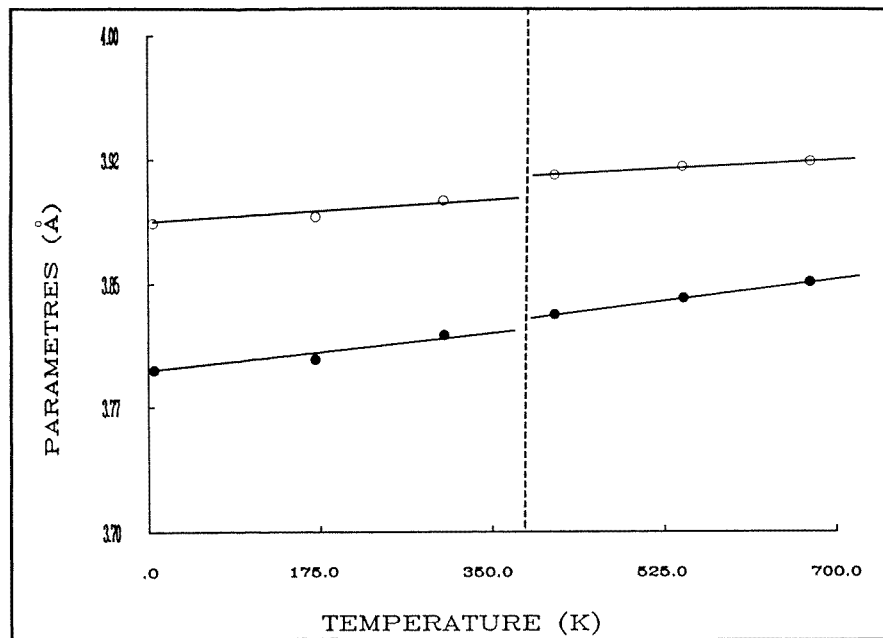
Figure 5. Evolution of the lattice parameters a (○) and b (●) of KFeF₄ versus temperature. Straight lines are just guides for the eyes.

Measurements have been performed on the D1A spectrometer, in the course of the nuclear study from 5 to 300 K. Figure 6 shows the neutron powder diffraction patterns of KFeF₄ collected at 170 K (above T_N) and 5 K. Below T_N magnetic diffraction lines appear, well separated from the nuclear ones; they are denoted by stars in figure 6(b). At least two of these lines bear witness to a doubling of the c parameter.

The cell parameters are then:

$$a_m = a_{II} \qquad b_m = b_{II} \qquad c_m = 2c_{II}.$$

In order to obtain a best resolution of the magnetic lines, we have collected a diffraction pattern on the DIB spectrometer with $\lambda = 1.91$ Å at 2 K. To predict the magnetic arrangement a model for the magnetic interactions in the plane can be considered by analogy with compounds presenting the same magnetic arrangement (RbFeF₄: Heger and Dachs 1972, Rb₂MnF₄: Breed 1967). This model lets us expect antiferromagnetic coupling with the magnetic moments of the Fe^{3+} ions in the plane perpendicular to the c axis. Elsewhere the doubling of the c parameters induces an antiferromagnetic coupling between Fe^{3+} ions aligned along the [001] direction. The layer planes containing these Fe^{3+} ions will be called second neighbour layer planes.

Refinement with only antiferromagnetic coupling between second neighbour layers was tested without success, several lines being observed but not predicted. The possibility of a weak canting of the moments away from the c direction, leading to the doubling of the c parameter, was investigated. Among the different possible cantings (Fe^{3+} are in general positions) only one represented in figure 7(a), different from the tilt of octahedra, takes into account all the principal lines but, as shown in figure 8(a) (star), a small line is predicted but not observed.
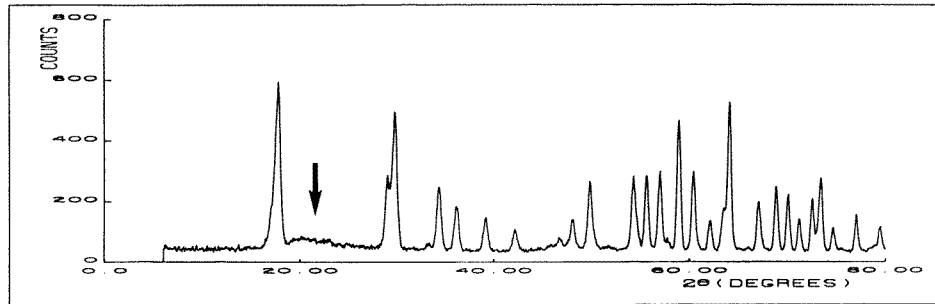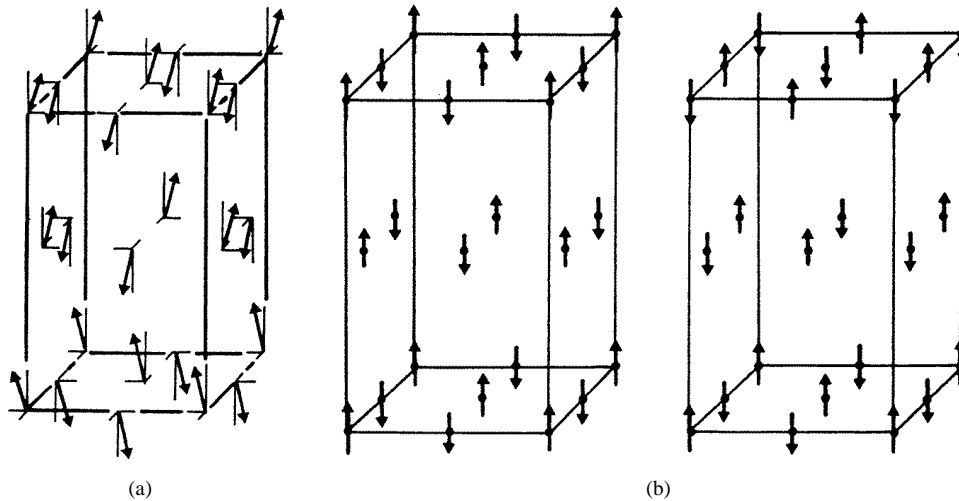
(a)
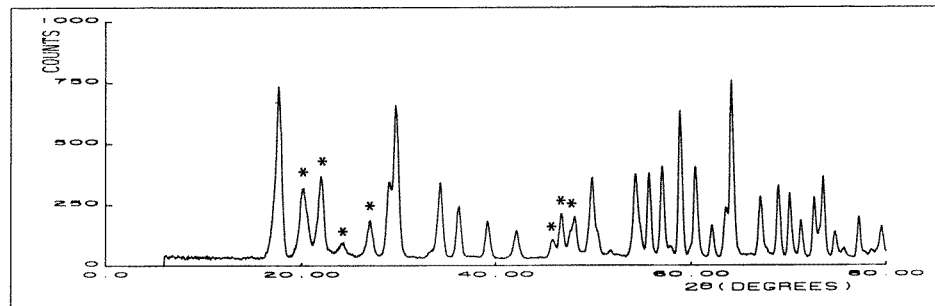
(b)

Figure 6. Neutron powder diffraction patterns of KFeF$_4$ collected on D1A at 170 K (a) and 5 K (b) with $\lambda = 1.916$ Å. The stars in (b) denote the magnetic lines. The arrow in (a) points out a broad signal observed in the angular range where the magnetic lines grow below T_N.


(a)   (b)

Figure 7. Magnetic arrangement: (a) in the hypothesis of a canting of the Fe^{3+} moments away from the c direction, (b) in considering two mixed patterns with ferromagnetic coupling (1) and antiferromagnetic coupling (2) between the moments which are aligned along the c axis.

Finally the best fit of the D1B data at 2 K is obtained by considering two mixed patterns of magnetic domains with $(a_{II}, b_{II}, 2c_{II})$ (the so-called 'antiferromagnetic phase')
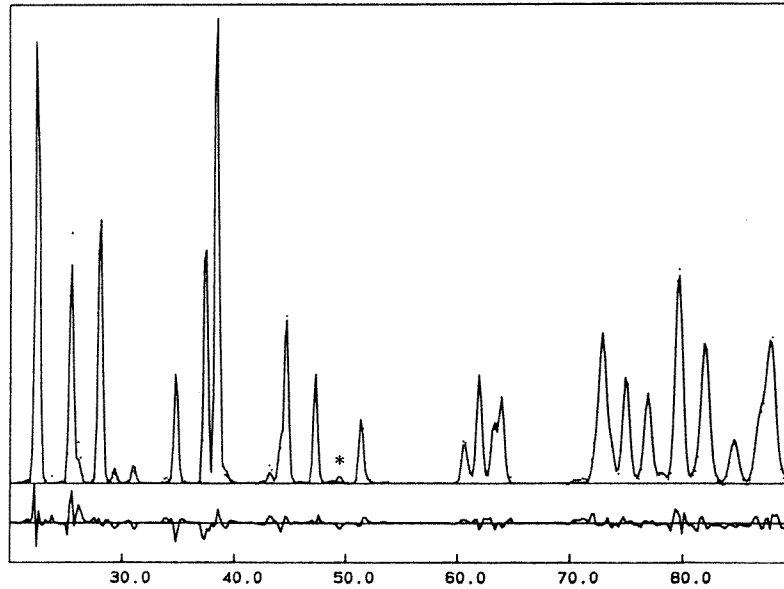
(a)
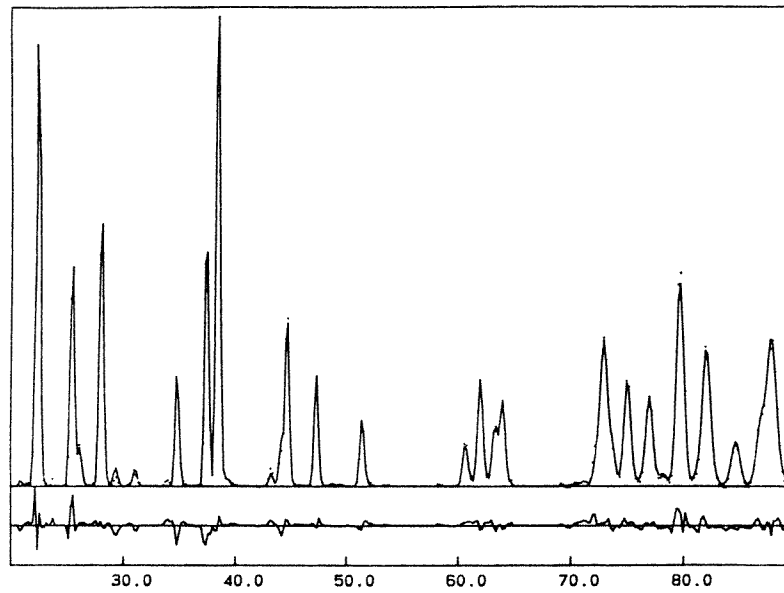
(b)

Figure 8. Observed (dotted curve) and calculated (full curve) patterns at 2 K with $\lambda 2.518$ Å(D1B) as described with two phases (b) or a single phase (a), involving a canting of the moments away from the c direction, with predicts an extra line not observed (star). The lower curves represent the difference patterns.

and (a_{II}, b_{II}, c_{II}) (ferromagnetic phase) cell parameters and magnetic moments along the c axis. These two phases are represented in figure 7(b). Figure 8(b) shows the observed and calculated diffraction patterns at 2 K. Parameters, atomic positions and isotropic thermal

motion parameters were taken from D1A data refinement at 5 K (from $6°$ to $160°$) in the nuclear cell with $a_m = 7.7626$ Å, $b_m = 7.5952$ Å and $c_m = 12.2558$ Å in the *Pcmn* space group. This procedure allows us to obtain accurate lattice data which can be compared with the nuclear ones. The results of the refinement are reported in table 4. The mean Fe–F distance is close to the value obtained in the non-magnetic phase.

Table 4. Reliability factors, lattice parameters and atomic coordinates in $KFeF_4$ at 2 K.

	R_{nuc}	R_{mag}	R_{prof}	μ_x	μ_y	μ_z	
1 phase	3.97	10.85	8.98	0.6(1)	1.28 (6)	3.80	
2 phases	5.27	8.12	9.80	0	0	0.59	Ferro. phase
				0	0	3.78	A. ferro. phase

T (K)	a_m	b_m	c_m
2 K	7.7626(7)	7.5952(2)	24.5116(6)

	x	y	z	B_{iso}
Fe	0.1230(7)	−0.0002(4)	0.1242(2)	0.29(3)
K_1	0.127(4)	0.25	0.4878(4)	0.42(7)
K_2	0.132(4)	0.75	0.2574(5)	0.42(7)
F_1	0.121(1)	0.0375(4)	0.3767(2)	0.59(5)
F_2	0.088(1)	0.25	0.1057(3)	0.52(6)
F_3	0.156(1)	0.75	0.1411(3)	0.52(6)
F_4	0.111(2)	0.049(1)	0.2000(2)	0.41(4)
F_5	0.128(2)	0.955(1)	0.0497(2)	0.41(4)

The estimated volume ratio between the two phases $P_{ferro}/P_{a.ferro} = 6.33$. We obtain for the Fe^{3+} magnetic moment the value of 3.78 μ_B. It can be noted that a large diffusion peak always exists at 2 K, around $2\vartheta = 40°$, under the: 110, 111, 112 and 113 magnetic diffraction lines, a magnetic disorder still subsists at 2 K. This phenomenon can explain the weak value find for the Fe^{3+} magnetic moment.

5. Discussion

These results show, in agreement with Heger *et al* (1971), that the magnetic structure of $KFeF_4$ can be described by an antiferromagnetic model in the layer planes (*ab*) with magnetic moments perpendicular to the planes. Below T_N, the long range magnetic order is established with c or $2c$ period structures; a three-dimensional antiferromagnetic structure by canted moments can be ruled out. However, two cases can be considered: (i) a mixed structure alternating ferromagnetic and antiferromagnetic coupling between the layer planes, (ii) a structure with ferro- and antiferromagnetic domains. Neutron diffraction cannot distinguish the two possibilities. Related magnetic behaviour has already been encountered in Rb_2MnF_4 (Ikeda *et al* 1987) with c, $2c$ and $3c$ period structures. The $3c$ long period structure is not observed in $KFeF_4$. At low temperature an interlayer magnetic disorder subsists in the crystal. We have noted also that precursor effects of the magnetic order have been observed during the neutron diffraction experiments to room temperature.

Acknowledgments

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