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Structural phase transitions in RbFeF_4 : I. Powder and single crystal x-ray diffraction study of the room temperature phase

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Abstract. A re-investigation of the room temperature phase of RbFeF_4 by single crystal and powder x-ray diffraction is presented. Using a Rietveld method for refinements, the space group is shown to be orthorhombic $D_{2h}^{11}-Pmab$ instead of $D_2^3-P2_12_12$ as proposed in the most recent work. As a result, the space group of the room temperature phase (phase IV) is not a subgroup of the space groups of the high temperature phases III ($D_{2h}^{13}-Pmmn$) and II (D_{4h}^5-P4/mbm). However, it obviously remains a subgroup of the highest temperature phase I (D_{4h}^3-P4/mmm). A 'discondensation' is deduced.

1. Introduction

The room temperature structure of the layer perovskite RbFeF_4 has been the object of a number of investigations. While Tressaud *et al* (1969) proposed the space group $C_{2v}^5-P2_1ab$, Abrahams and Bernstein (1972) found evidence for $D_{2h}^{11}-Pmab$ or $C_{2v}^5-P2_1ab$ and in the absence of second harmonic generation they retained the former though the latter gave better agreement between calculated and experimental diffraction intensities. Recently Hidaka *et al* (1986) have again investigated this structure by four circle single crystal diffractometry and proposed the non-centrosymmetric space group $D_2^3-P2_12_12$. It should be noted that the ionic coordinates of iron reported by Hidaka *et al* are not consistent with $D_2^3-P2_12_12$ symmetry, moreover the authors did not give the reasons for keeping the y coordinate fixed. Finally, from an electron diffraction study Deblieck *et al* (1985) found evidence for a doubling of the cell parameter perpendicular to the sheets. On the other hand RbFeF_4 is well known for its ferroelastic properties (Abrahams and Bernstein 1972). Ferroelastic domains are easily detected at room temperature on platelet crystals observed under polarized light.

The importance of the knowledge of the room temperature phase of RbFeF_4 comes from the point of view of the structural phase transitions (SPT) it undergoes. The $A^1M^{III}F_4$ layer compounds undergo different kinds of SPT, displacive SPT (Bulou and Nouet 1982), order-disorder SPT (Bulou *et al* 1982) and even martensitic SPT (Launay *et al* 1985).

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Table 1. Cell characteristics and conditions of intensity data collection and refinements.

Symmetry: Orthorhombic D_{2h}^1 - $Pmab$
Cell parameters (Å): $a = 7.6651(13)$, $b = 7.6316(15)$, $c = 6.2789(6)$
2θ range (°): 5–130
Step scan ($^{\circ}2\theta$): 0.04
Time/step (s): 25
Number of reflections: 341
Number of parameters: 30
Profile parameters: $U_1 = 0.40(5)$, $V_1 = -0.03(5)$, $W_1 = 0.14(1)$
for $a = 50$, $l = 24$: $U_2 = 0.6(4)$, $V_2 = -0.1(3)$, $W_2 = 1.43(6)$
(see equation (1)): $C = -0.024(3)$, $D = -0.28(1)$
Reliability factors (%): $R_1 = 6.48$, $R_p = 12.62$, $R_{wp} = 14.57$

RbFeF₄ exhibits three SPT at 923 K (Tressaud *et al* 1969), 416 K and 380 K (Hidaka *et al* 1986). Above 923 K (phase I) the compound has the ideal tetragonal structure with D_{4h}^1 - $P4/mmm$ symmetry (Tressaud *et al* 1969). Phase II belongs to the space group D_{4h}^5 - $P4/mbm$ (Hidaka *et al* 1986). A second order phase transition leads to phase III, space group D_{2h}^{13} - $Pmmn$ (Hidaka *et al* 1986). The room temperature phase which appears after a first order transition (Hidaka *et al* 1979) is denoted as phase IV. This latter transition, never encountered in the tetrafluoroaluminates, seems to indicate a new behaviour since according to the symmetries proposed in the literature, the space group of the room temperature phase is or is not a subgroup of the space groups of the high temperature phases III and II: the condensation responsible for the 923 K phase transition may disappear at 380 K. For this reason a knowledge of the space group of the room temperature phase is of special interest. This diffraction study has been performed in connection with a Raman scattering study (Pique *et al* 1990, part II of this work).

2. Experimental details

Powder samples were obtained by heating at 893 K for 48 h a stoichiometric mixture of RbF and FeF₃ in sealed gold tubes.

Single crystals were prepared by a hydrothermal synthesis method in which a stoichiometric mixture of RbF and FeF₃ in 10N HF was heated to 623 K for 48 h under autogenous pressure. Platelet colourless crystals were selected for performing x-ray diffraction and Raman scattering experiments.

X-ray powder diffractograms used for the structural determination were recorded on a Siemens D501 diffractometer (back-monochromatized Cu K α). The conditions of intensity data collection are shown in table 1.

Single crystal x-ray diffraction photographs were taken in a Weissenberg camera using Cu K α Ni-filtered radiation.

3. Results and discussion

Oscillation and Weissenberg photographs taken at room temperature around the axis normal to the layers give evidence for an orthorhombic cell: 7.69 Å, 7.64 Å, 6.33 Å. In

spite of a careful study we did not observe any line which could indicate a doubling of the *c* parameter as found by Deblieck *et al* (1985). As the cell parameters of the highest temperature phase are approximately $a = 3.85 \text{ \AA}$, $c = 6.29 \text{ \AA}$ (Tressaud *et al* 1969), this result implies a doubling of the intra-layer parameters.

The existence of ferroelastic domains and the very small difference between *a* and *b* have been taken into account for finding the space group. As a result, undoubted reflection conditions are: *hkl*: no conditions; *h00*: $h = 2n$; *0k0*: $k = 2n$; *00l*: no conditions; *hk0*: $k = 2n$ (in particular, reflections such as $h + k = 2n + 1$ are observed). Unfortunately, the reflection conditions for the *h0l* set of reflections are not so clear due to the presence of ferroelastic domains. In addition, absence of second harmonic generation, as reported by Abrahams and Bernstein (1972), indicates that a centrosymmetric space group should be more appropriate, that is a D_{2h} point symmetry in an orthorhombic system. With respect to the cell parameters given above, two space groups are compatible with all the information: D_{2h}^{11} -*Pmab* and D_{2h}^8 -*Pbab*. However, the existence of reflections *0kl*, $k \neq 2n$, which are forbidden for D_{2h}^8 -*Pbab* but permitted for D_{2h}^{11} -*Pmab* symmetry, reduces the number of permitted space groups to one.

Owing to the intrinsic multi-domain character of the crystals, an x-ray powder diffraction data set was chosen for refinements. The procedure used is a new version of a modified Rietveld method which describes the profiles by means of Fourier coefficients (Lartigue *et al* 1987, Gibaud *et al* 1986). The shape of any reflection at a given angle θ is approximated by:

$$g(x, \theta) = \frac{1}{a} \sum_{n=-l}^l \left(\exp(-H_\theta |n|^{T_\theta}) \cos \frac{2\pi nx}{a} + B_n \sin \frac{2\pi nx}{a} \right) \quad (1)$$

where $H_\theta = U_1 \tan^2 \theta + V_1 \tan \theta + W_1$ is related to the width of the reflection following the formulation of Caglioti *et al* (1958). The value of $T_\theta = U_2 \tan^2 \theta + V_2 \tan \theta + W_2$ directly influences the shape which can be Gaussian ($T = 2$), Cauchy-like ($T = 1$) or may be continuously intermediate. The asymmetry was found to be reasonably well reproduced by the following Fourier coefficients:

$$B_n = [1/(1 + \tan \theta)^2](Cn^2 + Dn) \exp(-n/2)$$

this empirical relation increases the total number of profile parameters to eight: $U_1, V_1, W_1, U_2, V_2, W_2, C$ and D .

3.1. Space group D_{2h}^{11} -*Pmab*

Cell parameters, conventional Rietveld reliability factors together with profile parameters are given in table 1 for space group D_{2h}^{11} -*Pmab*. The initial unit cell model was deduced from the symmetry relation with phase I. The observed and calculated patterns are presented in figure 1. There are two reflections which are not indexed by the model. They can be imputed to impurities since they cannot be explained by any orthorhombic lattice with $2a, 2b, c$ parameters (where a, b, c represent the cell parameters of the ideal phase I) and moreover they were not found in another x-ray powder diffractogram performed using a different sample.

The atomic coordinates are reported in table 2 while selected interatomic distances and angles are given in table 3. The structure consists of layers of FeF₆ corner-sharing octahedra separated by Rb atoms (figures 2 and 3). The coordination about the Fe atom is close to octahedral with deviations from this symmetry less than 2.3°. The longer Fe–

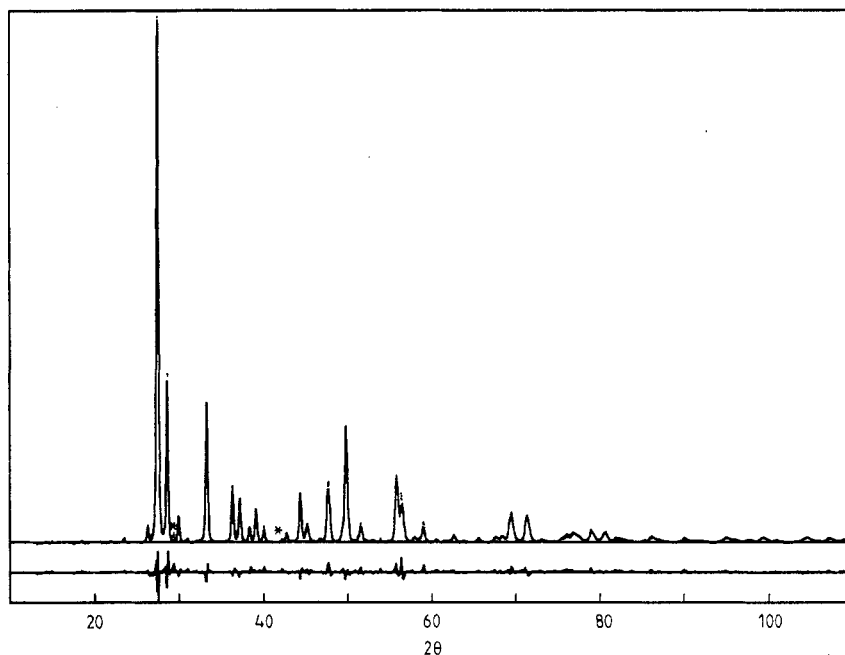


Figure 1. Comparison of observed (dotted curve) and calculated (full curve) intensities of RbFeF_4 . The difference pattern appears below on the same scale. Asterisks correspond to impurities.

Table 2. Atomic coordinates and thermal parameters[†] in RbFeF_4 room temperature phase (space group $D_{2h}^{17}-Pmab$). Standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}
Fe	0	0	0	0.51(5)	$\beta_{22} = \beta_{11}\ddagger$	0.45(12)
Rb	1/4	0.2824(2)	0.5136(5)	1.34(4)	$\beta_{22} = \beta_{11}\ddagger$	0.48(8)
$F_{1(\text{eq})}$	0	1/4	-0.0711(22)	2.58(19)	0.34(15)	0.43(26)
$F_{2(\text{eq})}$	1/4	-0.0093(10)	-0.0630(22)	$\beta_{22}(F_1)\ddagger$	$\beta_{11}(F_1)\ddagger$	$\beta_{33}(F_1)\ddagger$
$F_{3(\text{ax})}$	0.0410(9)	0.0497(9)	0.2889(9)	0.18(10)	$\beta_{22} = \beta_{11}\ddagger$	1.42(19)

[†] Thermal parameters β_{ij} ($\times 10^2$) relate to the expression: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2)]$.

[‡] Fixed (see text).

Table 3. Selected interatomic distances (Å) and angles (°) in RbFeF_4 room temperature phase. Standard deviations are given in parentheses.

Fe- $F_{1(\text{eq})}$	$2 \times 1.959(3)$	F_1 -Fe- F_2	$2 \times 89.4(3)$	$\langle \text{Fe-F} \rangle = 1.93$
Fe- $F_{2(\text{eq})}$	$2 \times 1.958(3)$		$2 \times 90.6(3)$	
Fe- $F_{3(\text{ax})}$	$2 \times 1.880(6)$	F_1 -Fe- F_3	$2 \times 88.6(4)$	
F_1 -Fe- F_1	180.0(0)	F_2 -Fe- F_3	$2 \times 91.3(4)$	
F_2 -Fe- F_2	180.0(0)		$2 \times 87.8(4)$	
F_3 -Fe- F_3	180.0(0)		$2 \times 92.2(4)$	

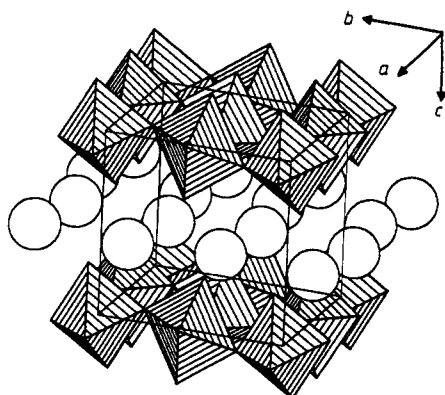


Figure 2. View of the room temperature unit cell of RbFeF₄ showing the layered character of this compound. Open circles stand for Rb atoms and octahedra for FeF₆ units.

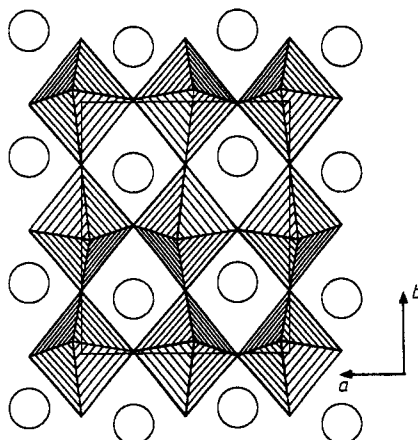


Figure 3. (001) view of the room temperature unit cell of RbFeF₄ showing the connection between FeF₆ octahedra in a layer and the interstitial position of Rb atoms represented by open circles.

F distances are relative to the shared fluorine atoms, the mean Fe–F distance being very close to the sum of the ionic radii (Shannon 1976). The tilt angle φ_a (around the $[100]$ axis) is 12° as deduced from the $F_{(\text{eq})}$ or $F_{(\text{ax})}$ displacements. On the other hand the value of φ_b (around the $[010]$ axis) is 13° when taken from $F_{(\text{eq})}$ but only 10° when taken from the $F_{(\text{ax})}$ displacements, which indicate an octahedra distortion. No rotation is detected about the c axis. It can be noted that the tilt angles φ_a and φ_b are large with respect to those encountered in the tetrafluoroaluminates (Bulou and Nouet 1982, 1987), being in agreement with the large intensities observed on the Raman spectrum (Pique *et al* 1990). The thermal parameters are reported in table 2. Considering the small distortion arising from the SPT phase I–phase IV which can be explained just by a tilting of the octahedra, $a^\circ b^\circ c^\circ$ for phase I (Tressaud *et al* 1969, Pique *et al* 1990) and $a_p^+ b_p^- c^\circ$ for phase IV in the Glazer–Bulou notation (Glazer 1975, Bulou and Nouet 1982), the symmetry of phase I, D_{2h}^1-P4/mmm , has been argued for the anisotropic temperature factors in order to avoid a too large and physically meaningless number of refined parameters. A similar approximation has been applied to RbAlF₄ by Bulou and Nouet (1982).

3.2. Space group $C_{2v}^5-P2_1ab$

The reported reflection conditions are also consistent with a non-centrosymmetric space group C_{2v}^5 since systematic extinctions are the same for either D_{2h}^1-Pmab or $C_{2v}^5-P2_1ab$ symmetry. However, C_{2v}^5 is unlikely to be the correct space group for the room temperature phase owing to the following experimental results:

- (i) Second harmonic generation was not detected (Abrahams and Bernstein 1972).
- (ii) The Raman scattering spectrum presents less lines than expected for the non-centrosymmetric space group (Pique *et al* 1990).
- (iii) Refinements using space group $C_{2v}^5-P2_1ab$ give the following results: $R_1 = 6.12$, $R_p = 12.72$, $R_{wp} = 14.77$. The initial model was taken from that found on D_{2h}^1-Pmab since the first is a subgroup of the second. The reliability factors are lower than those calculated for D_{2h}^1 symmetry but the slight decrease cannot be considered significant

enough (Hamilton 1964). In addition, the octahedron is more distorted considering space group $C_{2v}^5-P2_1ab$ than $D_{2h}^{11}-Pmab$. As an example the angles F–Fe–F range from 86° up to 97° and the distances Fe–F from 2.2 \AA down to 1.7 \AA . Such an unusual distortion makes the $C_{2v}^5-P2_1ab$ symmetry less appropriate than the $D_{2h}^{11}-Pmab$ one.

3.3. Space group $D_2^3-P2_12_12$

Phase IV ($D_{2h}^{11}-Pmab$) is neither a subgroup of phase III ($D_{2h}^{13}-Pmmn$) nor of phase II (D_{4h}^5-P4/mbm). On the other hand Hidaka *et al* (1986) proposed the $D_2^3-P2_12_12$ space group for the room temperature phase which is a subgroup of the space groups of phases III and II. This solution has been checked but it appears not to be consistent with these experimental results:

(i) On the oscillation and Weissenberg photographs none of the $hk0$ $k \neq 2n$ reflections forbidden in $D_{2h}^{11}-Pmab$ symmetry but permitted in $D_2^3-P2_12_12$ are observed. No reflection conditions are reported by Hidaka *et al* (1986).

(ii) Refinements using the space group $D_2^3-P2_12_12$ give the following Rietveld reliability factors: $R_1 = 12.08$, $R_p = 20.51$, $R_{wp} = 22.78$. Hidaka's model has been taken as the initial one for refinements but the coordinate y of iron has not been fixed, as Hidaka does, because this is not consistent with the $D_2^3-P2_12_12$ symmetry.

(iii) Moreover the absence of second harmonic generation (Abrahams and Bernstein 1972) is an additional indication for a centrosymmetric space group while $D_2^3-P2_12_12$ is not.

3.4. Space group $C_{2h}^2-P2_1/m$

If $D_{2h}^{11}-Pmab$ is accepted as the correct space group, it is convenient to check a subgroup which maintains the condensation responsible for the 923 K phase transition at room temperature. The monoclinic space group $C_{2h}^2-P2_1/m$ (setting $P2_1/m11$) fulfils this condition since this centrosymmetric space group is a subgroup of the space groups of phases III, II and I. The following reasons are contrary to this proposal:

(i) Oscillation and Weissenberg photographs give no evidence of monoclinic arrangement of the atoms. However, small differences from orthorhombic symmetry are not likely to be detectable in photographic data.

(ii) Oscillation and Weissenberg photographs do not evidence any of the $0k0$ $k \neq 2n$ reflections. These reflections are forbidden in $D_{2h}^{11}-Pmab$ symmetry but permitted in $C_{2h}^2-P2_1/m$ (setting $P2_1/m11$).

(iii) Refinements using space group $C_{2h}^2-P2_1/m$ give the following Rietveld reliability factors: $R_1 = 7.86$, $R_p = 14.37$, $R_{wp} = 16.74$. Initial atomic coordinates have been deduced from those found on $D_{2h}^{11}-Pmab$ symmetry since $C_{2h}^2-P2_1/m$ (setting $P2_1/m11$) is a subgroup of $D_{2h}^{11}-Pmab$. Moreover the octahedron is more distorted considering the space group C_{2h}^2 than D_{2h}^{11} . As an example the angles F–Fe–F range from 94° down to 86° and the distance Fe–F from 1.7 \AA up to 2.1 \AA , which makes the C_{2h}^2 symmetry less appropriate than D_{2h}^{11} .

4. Conclusions

Unlike the latest literature report, the space group $D_{2h}^{11}-Pmab$ can be regarded as the correct one determining the arrangement of atoms in the room temperature phase of

RbFeF₄. As a result phase IV is not a subgroup of the space groups of the high temperature phases III (D_{2h}^{13} - $Pmmn$) and II (D_{4h}^5 - $P4/mbm$). However, it obviously remains a subgroup of phase I (D_{4h}^1 - $P4/mmm$). Then the condensation responsible for the 923 K SPT exists in phase II and still in phase III but disappears at room temperature, which is uncommon. Phase IV can be described in Glazer–Bulou notation (Glazer 1975, Bulou and Nouet 1982) by the tilt system $a_p^+ b_p^- c^0$, while in phase III the tilt system is $a_p^+ b_p^+ c^+$. Note that according to Hidaka *et al* (1986) the tilt angle around the c axis begins to decrease in phase III as revealed by the behaviour of the 5/2 3/2 1 line intensity.

Baumeler *et al* (1984) pointed out the fact that the transition at 380 K should not be truly first-order in character but a 'weak' first order SPT (Müller 1981) since the room temperature phase IV (D_2^3 - $P2_12_12$) was still a subgroup of the high-temperature phase III (D_{2h}^{13} - $Pmmn$). The present results with D_{2h}^{11} - $Pmab$ space group for room temperature phase, establish that this 380 K SPT cannot be a second-order one.

Acknowledgments

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