Four-dimensional description of the structure and phase transitions of $KFeF_4$ (phase II and superstructure phase III)

Ph. Sciau* and D. Grebille
Laboratoire de Chimie-Physique du Solide, Ecole Centrale Paris, Grande Voie des Vignes, 92295 Chatenay Malabry, CEDEX, France
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The structural phase transitions of $KFeF_4$ have been investigated by x-ray powder and monocrystal techniques. Dilatometric experiments have allowed us to characterize the transition between the so-called phase II and the twofold superstructure phase III. It is accompanied by a contraction of the a and b parameters, which is compatible with a rotation of the FeF_6 octahedra around the c axis, and by an anomaly along the c direction, 10 K above the previous transition temperature. To investigate the phase transition II→III, structural characterization of the two phases II and III has been achieved. Preliminary classical studies had shown that the related symmetry space groups were, respectively, *Amma* and *Pmcn*. A new structural four-dimensional investigation, which considers phase III as a modulated structure of the average of phase II, has confirmed these first results. The superspace group is $P^{A\,mma}_{1\,\bar{1}\,s}$ and the real structure corresponds to the section $t=\frac{1}{8}$ of the supercrystal. The structural refinement of the structure leads to an R factor of 0.046 for 31 refinement parameters. The atomic displacements are consistent with a rigid-body rotation of the FeF_6 octahedra in agreement with the dilatometric-powder study. Moreover, the four-dimensional method has proved to be more rigorous to take into account the real symmetry of phase III, to describe more correctly the diffraction pattern, and to be more efficient in refining the structure with fewer refinement parameters. We have shown that the phase transition II→III is also compatible with the Landau theory for structural, continuous phase transitions, which allowed us to derive the symmetry of the modulated structure of phase III. $KFeF_4$ is proved to be a good example first to prove the usefulness of the four-dimensional analysis for a superstructure considered as a commensurate modulated structure, and second, to make a useful comparison between the superspace theory and the Landau theory of the invariance of the free-energy expansion.

I. INTRODUCTION

The ABX_4 layer compounds have been the subject of many investigations. The structures of these perovskite-related compounds consist of two-dimensional (2D) networks of BX_6 octahedra connected by the A cations. They are usually characterized by displacive phase transitions featuring tilting of complete undistorted octahedra. For compounds such as $TlAlF_4$ or $RbFeF_4$, for which the centers of the octahedra are aligned along the c axis (axis perpendicular to the layers), a classification of the different phases[1] and a group analysis of the phase transitions[2] have been given. The aristotype phase (phase with the highest possible symmetry[3]) of this structural family is shown in Fig. 1(a).

In this paper, we are interested in the compounds of the KMF_4 series (with M=Fe, Ti, and V). Their aristotype phase is different from the previous one: here, an octahedra layer is translated by half of a basic translation (**a** or **b** following the choice of axis in layers) from the neighboring one [Fig. 1(b)]. Its symmetry is orthorhombic with an A-face centering (or B). In the study of $KFeF_4$, our purpose is to show that a four-dimensional treatment,[4] which has been particularly successful in the symmetry description and structural determination of incommensurate modulated phases,[5] is adequate for the description of the phase III of those compounds. It allows us to keep the A centering which is lost in the classical three-dimensional structural study and gives a better description of the crystal symmetry.

According to Hidaka *et al.*,[6] $KFeF_4$ has two structural phase transitions: A first-order transition occurs at 563 K between the so-called phase I (aristotype phase) and phase II (space group *Amma*). A second transition at about $T_i=370$ K is reported to be continuous and leads to a primitive orthorhombic phase (phase III of the proposed space group *Pmmn*). It is accompanied by a doubling of the b parameter. Only this last one exists in $KTiF_4$ and KVF_4, respectively at about 490 and 530 K; moreover, in these compounds, it has been supposed to be a first-order one. In the precise study of the $KFeF_4$ transition II→III,[7,8] it has been observed that the intensity of the superstructure reflections is still nonzero above the transition temperature T_i and vanishes only at 10 or 15 K above T_i. Furthermore, the linewidth remains constant up to 10 or 15 K above T_i and then increases, and the authors have considered the possibility of a double transition.

In order to confirm the structures of $KFeF_4$, a previous study[9] has allowed us to solve and to describe the struc-

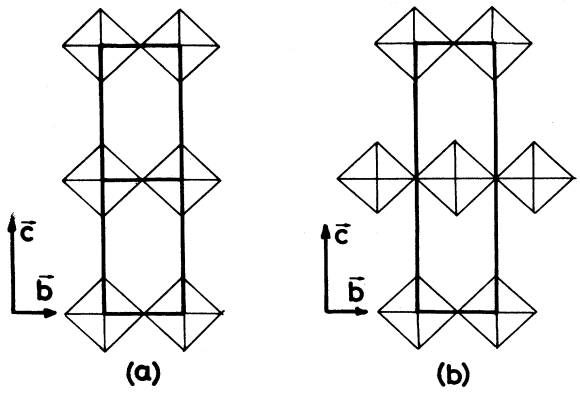

FIG. 1. Schematic representation of the aristotype phase of the structural family of (a) $TlAlF_4$ and (b) KMF_4 series (M=Fe, Ti, or V).

tures of phases II and III by the classical methods (crystallographic space groups of R^3). The structure of phase II (space group *Amma* with a=7.68 Å, b=3.92 Å, c=12.39 Å, Fig. 2) agrees with the assumed one[6] and can be related to Heger's study.[10] But it is not true for phase III (space group *Pmcn*, $\mathbf{a}'=\mathbf{a}$, $\mathbf{b}'=2\mathbf{b}$, $\mathbf{c}'=\mathbf{c}$): this space group does not agree with the group *Pmmn*, proposed by Hidaka, and with the conclusion given by Saint-Grégoire using the Landau theory.[7,11] According to our structural refinement, the symmetry reduction during the transition II→III results from the tilting of all FeF_6 octahedra about the c axis [$a^0b^+c^+$ for all the (FeF_6) layers in a notation of the two-dimensional networks adapted from Glazer's notations[12]], while the structure proposed by Hidaka would result from a tilting about the **a** axis of the only octahedra at z=0 (and not at $z=\frac{1}{2}$) ($a^+b^+c^0$ for the layers at z=0 and $a^0b^+c^0$ at $z=\frac{1}{2}$). Our structural description in the *Pmcn* space group is compatible with

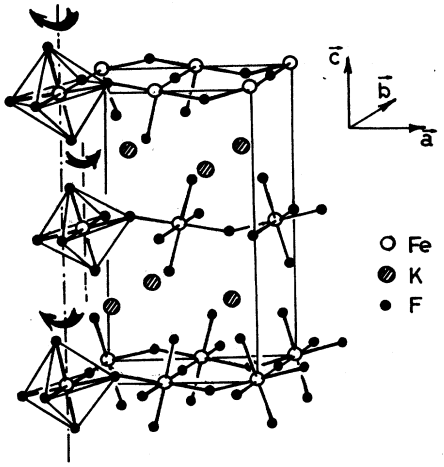

FIG. 2. Schematic representation of the structure of phase II of $KFeF_4$. Arrows indicate the tilting of the octahedra at the transition II→III.

the previous description of $KTiF_4$ at room temperature.[13] Those compounds are really isostructural.

Nevertheless, even with a good agreement factor, this result is not quite satisfactory. We have observed in the diffraction pattern of this phase a systematic extinction condition which is not explained by either the space group *Pmcn* or by any other space group of R^3. In this paper we shall show that this condition agrees with a symmetry operation of a superspace group, providing it is possible to distinguish main and satellite reflections. This last assumption is confirmed by the consideration of the relative intensities of the diffraction reflections. Then, we shall show that the 4D structural description is compatible with the classical one using the *Pmcn* space group and uses fewer refinement parameters.

These new structural conclusions induce a new characterization of the filiation of the different phases of $KFeF_4$. In order to get a general view of this phase sequence, we have also tried to put in evidence the high-temperature phase transition I→II and the existence of a high-temperature aristotype phase. Preliminary studies have been performed by the powder diffraction technique. Thermal expansion of $KFeF_4$ has been precisely studied; on the one hand, we could not find any phase I at high temperature before decomposition; on the other hand, the evolution of the cell parameters as a function of the temperature is a good complement to the study of the transition II→III and has confirmed the duality of this last transition. We shall first present these preliminary results (Sec. II). Then we shall describe the four-dimensional description and structural refinement of the phase III (Sec. III). Last, we shall discuss the symmetry consequences concerning the phase transition and the validity of the Landau theory in the present case (Sec. IV).

II. DILATOMETRIC STUDY OF $KFeF_4$ POWDER

A. Experimental conditions

$KFeF_4$ powder was obtained by the hydrothermal diffusion technique: FeF_3 is introduced with KF into a gold tube. The solvent is pure dilute HF. The crystallization conditions are realized with a temperature about 470 K and a pressure of 4×10^6 Pa.

X-ray powder patterns were recorded with Cu $K\alpha$ radiation using a rotating anode on a high-accuracy goniometer ($\Delta\theta=10^{-3}$°). The sample was placed in a furnace under helium pressure to avoid decomposition at higher temperatures. The patterns were recorded from room temperature up to 620 K. At this last temperature, the sample began to decompose. Lattice parameters were calculated using at least 15 lines at each temperature.

B. Results

Lattice parameters have been determined and are given in Fig. 3 as a function of the temperature from room temperature up to 620 K. These curves clearly exhibit two temperature ranges.

(1) $T>410$ K. We observe a regular and linear dependence of the three parameters a, b, and c on the tempera-

ture, which can be approximated with a very good accuracy by the following relations:

$$a=(0.142\times10^{-3})T+7.587\ ,$$
$$b=(0.0335\times10^{-3})T+3.8923\ , \quad (1)$$
$$c=(0.441\times10^{-3})T+12.140\ .$$

A preliminary experiment has shown a general decrease of x-ray intensities above 570 K which is related to the decomposition of the sample under usual atmospheric conditions. In order to investigate the eventual high-temperature phase transition I→II, the sample has been heated under helium pressure up to 620 K and we could not observe any anomaly in the dilatometric curves. In Hidaka's description, the transition I→II is characterized by the doubling of the a parameter and phase II appears as a twofold superstructure of the phase I; consequently, the lines (hkl) with odd h should vanish at the transition. We could not show any change in the relative intensity or linewidth of these lines, and so we could not find any evidence for the existence of the hypothetical phase I.

(2) $T<410$ K. We observe a discontinuity of the slope of the dilatometric curves, respectively, at 395 K for the a and b parameters at 408 K for the c parameter. These features clearly refer to the phase transition II→III, but with two characteristic temperatures. The evolution of the a and b parameters are similar and outline a contraction of the structure along the corresponding axes. This evolution is in good agreement with the involved rotation of the FeF_6 octahedra around the **c** axis, as it was described elsewhere,[9] and as it will be discussed in Sec. V.

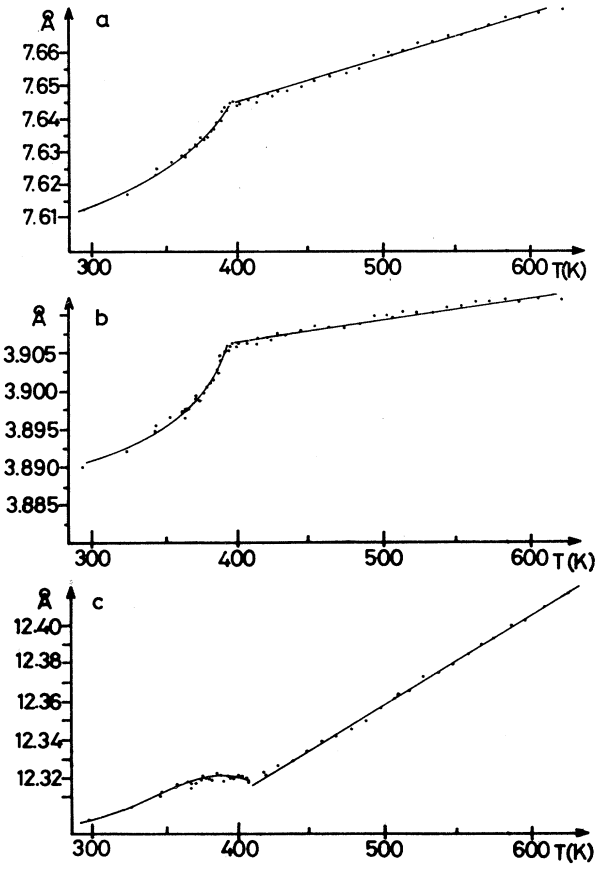

FIG. 3. Evolution of the lattice parameters of $KFeF_4$ vs temperature.

As far as the c parameter is concerned, the temperature characterizing the slope discontinuity is higher (408 K) and we observe an enhancement of the cell along the z axis from phase II to phase III, which cannot be directly correlated to the rotation of the FeF_6 octahedra. Our results confirm the hypothesis of a double transition: a first one at 408 K and a second one at 395 K. The first one has also been reported by Saint-Grégoire[7] from diffractometric results (intensity of the superstructure lines) and is related to the doubling of the b parameter. Nevertheless, we do not observe, at this temperature, any anomaly in the evolution of the b parameter in our dilatometric curves, and therefore any evidence of the rotation of the octahedra. This first transition seems to be characterized by a structural distortion along the **c** axis with a doubling of the translation period along the **b** axis.

We could not show, in the powder diffraction patterns, any discontinuity of the intensity or the linewidth of the reflections around the transition II→III. This confirms the quasicontinuous character of this transition and will justify the description of the phase transition by the Landau theory of second-order transitions.

III. 4D DESCRIPTION OF PHASE III

In this section, we shall describe the structure of phase III using the monocrystal diffraction data obtained from our preceding structural study,[9] and using the superspace symmetry description.

A. Symmetry superspace group

As far as stronger reflections are concerned, the diffraction pattern of phase III is similar to phase II [reciprocal cell $(\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*)$]. But one can also observe very weak superstructure reflections located at $(0,\pm\frac{1}{2},0)$ from stronger reflections (Fig. 4). Below the transition, there is no loosening of the extinction condition of phase II (A centering).

In a 3D treatment [Fig. 4(b)], one doubles the b parameter to index all the reflections.[9] The new cell is

$$(\mathbf{a}',\mathbf{b}',\mathbf{c}') \text{ with } \mathbf{a}'=\mathbf{a},\ \mathbf{b}'=2\mathbf{b},\ \mathbf{c}'=\mathbf{c}\ . \quad (2)$$

It is a primitive cell. However, one can see in Fig. 4(b) that the reflections of the (hkl) type with k even are in agreement with an extinction rule (which corresponds to the A centering of phase II) but the reflections (hkl) with k odd (superstructure reflections) do not follow this rule, and this extinction leads to the reflection condition

$$(hkl) \text{ with } k \text{ even: } k+2l=4n\ . \quad (3)$$

It does not agree with any symmetry operation of a 3D space group: this condition cannot be considered in this

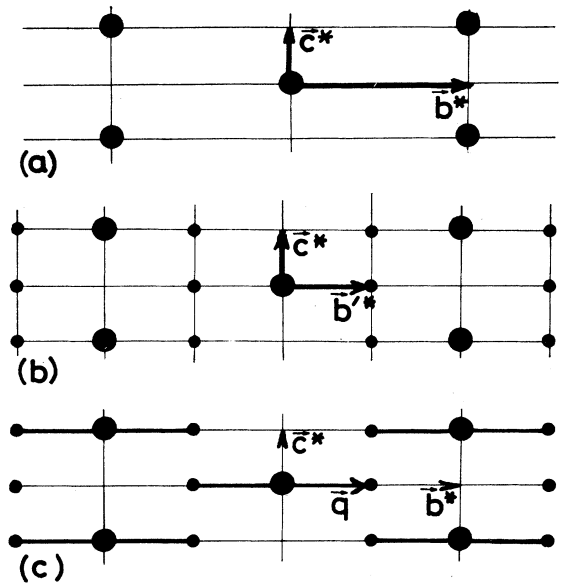

FIG. 4. Schematic representation of the $(0kl)$ plane of the diffraction pattern of $KFeF_4$: (a) phase II, (b) phase III in the superstructure cell, (c) phase III in the cell of the basic structure, modulated by a $\mathbf{q}$ vector.

classical treatment. Moreover, no difference between superstructure reflections and stronger reflections (on the nodes of phase II) is taken into account in the interpretation of the diffraction pattern.

Now, if we want to take into account the respective intensities of the superstructure and main reflections, we can consider phase III as a modulated phase of phase II with a commensurate wave vector $\mathbf{q}=\frac{1}{2}\mathbf{b}^*$, and it will be possible to use the $(3+d)$-dimensional approach developed by de Wolff, Janner, and Janssen.[4,14]

The modulated structure admits for basic structure the structure of phase II. Then, all reflections can be indexed by four integers [Fig. 4(c)]:

$$\mathbf{S}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{q} \ . \tag{4}$$

The stronger (or main) reflections are indexed with $m=0$ and define the basic structure of the modulated phase. The weaker reflections of the superstructure, or satellite reflections, are given by $m=\pm 1$. Their intensities are related to the difference of electronic density between the modulated and basic structures, and so allow us to calculate the atomic displacements from the average atomic positions. If we now consider each group of reflections $m=0$ and $m=\pm 1$ as a whole, we recover a centered diffraction pattern.

The 4D lattices are now generated by the following basis vectors[4] in the reciprocal space:

$$\begin{aligned}\mathbf{a}_1^*&=\mathbf{a}^* \ ,\\ \mathbf{a}_2^*&=\mathbf{b}^* \ ,\\ \mathbf{a}_3^*&=\mathbf{c}^* \ ,\\ \mathbf{a}_4^*&=\mathbf{e}_4^*+\mathbf{q} \ ,\end{aligned} \tag{5}$$

and in the direct space

$$\begin{aligned}\mathbf{a}_1&=\mathbf{a} \ ,\\ \mathbf{a}_2&=\mathbf{b}-\mathbf{e}_4/2 \ ,\\ \mathbf{a}_3&=\mathbf{c} \ ,\\ \mathbf{a}_4&=\mathbf{e}_4 \ ,\end{aligned} \tag{6}$$

where $\mathbf{e}_4$ and $\mathbf{e}_4^*$ are, respectively, the unit vectors orthogonal to R^3 and to R^{3*}.

The reflection condition (3) becomes

$$(hklm), \ k+1=2n \ .$$

Now it corresponds to the centering translation $(\mathbf{a}_2+\mathbf{a}_3)/2$ in the supercell. The corresponding 4D Bravais class is $P\,{}^{Ammm}_{1\,\bar{1}\,1}$ (de Wolff, Janssen, and Janner's notation[14]) or $P2\perp 2,m,m$ (Weigel, Phan, and Veysseyre's notation[15]).

We can outline here that, what we have called until now, systematic extinction for the vanished nodes of the high-temperature phase cannot be a rigorous one. These nodes correspond to main reflections and to second-order satellites of our modulated structure. The extinction rule is only valid for main reflections and it could be possible to measure a weak intensity corresponding to the satellites. In a 3D description, it is not possible to make the distinction between these different reflections, and it is why we cannot speak of a real extinction. However in a 4D description, we can explain the eventual very weak intensity of these nodes only by the existence of second-order satellites and so, we can speak of a real extinction condition: $(hklm)$, $h+1=2n$.

The diffraction pattern of the basic structure coincides with the pattern of the high-temperature phase II. So, we have chosen the space group $(Amma)$ as group of the basic structure, and we obtain four possible superspace groups:

$$P\,{}^{Amma}_{1\,\bar{1}\,1}, \ P\,{}^{Amma}_{s\,\bar{1}\,1}, \ P\,{}^{Amma}_{s\,\bar{1}\,s}, \text{ and } P\,{}^{Amma}_{1\,\bar{1}\,s} \ .$$

The other reflection conditions which are observed on the diffraction pattern ($hk0m$: $h+m=2n$ and no condition for $0klm$) lead to the group $P\,{}^{Amma}_{1\,\bar{1}\,s}$.

The real structure is a section of the supercrystal perpendicular to the fourth coordinate axis[14] (internal coordinate). When the modulation vector is incommensurate, the different sections of the supercrystal are all equivalent and correspond to different arbitrary phase shifts of the modulation wave.

For commensurate modulations, different sections by the 3D space refer to different 3D structures. The first step is to determine the good one, which corresponds to the real structure.[16] We can characterize these different sections by their coordinate t along the fourth direction, which also characterizes the phase shift of the modulation wave.

Those different 3D sections of a 4D structure have different 3D-space groups since the modulation is commensurate and since each section keeps a translational symmetry group, which is a subgroup of the basic structure one. The difference between them is reflected by the

different 3D groups involved, which are different restrictions of the 4D-group to the physical 3D space. All their symmetry elements $(R/\mathbf{v})$, where R is a 3×3 matrix and $\mathbf{v}$ a translation 3D vector, are the restrictions to R^3 of the supergroup operators $(R,\epsilon/\mathbf{v},\tau)$. Those which are conserved within the physical space (the 3D section of the supercrystal) must leave this 3D-space invariant, and consequently, their translational component $(\mathbf{v},\tau)$ must belong to the 3D section. So it must fulfill the following condition:[17]

$$\mathbf{q}\cdot\mathbf{v}=\tau\ . \tag{7}$$

Using this condition it is possible to determine the 3D groups for each section of the superspace group $P^{Amma}_{1\,\bar{1}\,s}$ (Fig. 5).

The operators with $\epsilon=+1$ have a τ value independent of the choice of the origin along the fourth dimension; they will be operators of the 3D group or not, independently of the choice of the origin, i.e., independently of the chosen section. But for the operators with $\epsilon=-1$, the τ values depend on the choice of this origin and these operators belong to the 3D-space group only for a particular set of 3D sections.

In our case, the operators with $\epsilon=+1$ which fulfill the condition (7) define a 3D-space group $Pm2_1n$ [in the cell $(\mathbf{a},2\mathbf{b},\mathbf{c})$]. The A centering $(\mathbf{a}_2+\mathbf{a}_3)/2$ of the supercell is not a vector of the 3D space, and therefore, it is not a symmetry element of the 3D-space group of the superstructure. This also explains why the corresponding extinction condition is not a possible one in a classical analysis.

The τ value of the other operators depends on the choice of the section. For example, if the origin is chosen so that the τ value of the element (m_y) is zero this element is $(m_y,1/0,0,0,0)$ and it is kept in the section given by $t=0$ (Fig. 5). For this section, the 3D-space group is $P2_1/m\ 2_1/m\ 2/n$ $(Pmmn)$. On the other hand, if we consider the section $t=\frac{1}{8}$, the τ value of the mirror plane m_y becomes $\frac{1}{4}$; this element is not kept but the element $(m_y,1/0,\frac{1}{2},\frac{1}{2},\frac{1}{4})$ (product of m_y by the A centering) is kept and becomes a glide mirror c. The 3D group of the section $t=\frac{1}{8}$ is $P2_1/m\ 2_1/c\ 2_1/n$ $(Pmcn)$. Considering all the sections, one obtains the results of Table I. For all the other sections there are no elements with $\epsilon=-1$ and the space group is $Pm2_1n$.

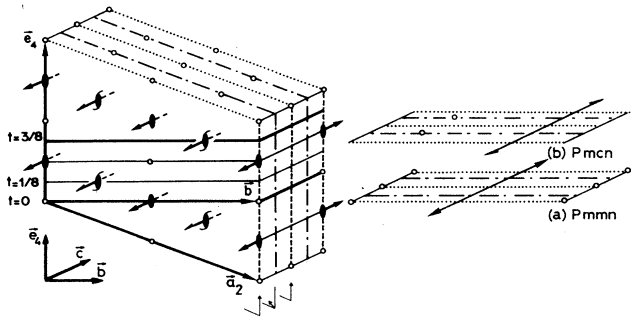

FIG. 5. Schematic representation of the section of the superspace group $P^{Amma}_{1\,\bar{1}\,s}$ by the $\mathbf{b},\mathbf{c},\mathbf{e}_4$ hyperplane and of its different 3D sections by the physical space. One can recognize, respectively, in (a) and (b) the sections $\mathbf{b},\mathbf{c}$ of the half-cells of the 3D-space groups $Pmmn$ and $Pmcn$.

TABLE I. 3D-space groups of the different sections of the superspace group $P^{Amma}_{1\,\bar{1}\,s}$.

t	Space group [cell $(\mathbf{a},2\mathbf{b},\mathbf{c})$]
$=0\ \mathrm{mod}(\frac{1}{4})$	$P2_1/m\ 2_1/m\ 2/n$
$=\frac{1}{8}\ \mathrm{mod}(\frac{1}{4})$	$P2_1/m\ 2_1/c\ 2_1/n$
$\neq0\ \mathrm{mod}(\frac{1}{8})$	$Pm2_1n$

To be consistent with the preceding 3D structure refinement, we have to choose the section $t=\frac{1}{8}$ or $\frac{3}{8}$ for our 4D analysis. We can confirm this choice by refining the structure in its 4D symmetry description and this will allow us to outline the advantages of such an analysis.

B. Structure

We have just seen that the real structure is the section $t=\frac{1}{8}$ or $\frac{3}{8}$ of the supercrystal. In fact, the 3D structures of these two sections are equivalent. One can deduce the second one from the first one by a translation of the origin of $(\mathbf{b}+\mathbf{c})/2$. In the following, we have chosen the section $t=\frac{1}{8}$. The least-squares refinement program REMOS (Ref. 18) works in this 4D description but in the section $t=0$. Consequently, we have translated the cell origin along the fourth axis by a vector $\frac{1}{8}$. The symmetry elements of superspace group $P^{Amma}_{1\,\bar{1}\,s}$ are given in Table II for the preceding choice of the origin.

The displacive modulation u^μ of the μth atom is defined by the atomic displacement coordinates u_l^μ from the average position $\bar{x}_l^\mu$:

$$u_l^\mu=x_l^\mu-\bar{x}_l^\mu\quad(i=1,2,3)\ . \tag{8}$$

In the 4D treatment, these displacements are periodic functions of the fourth variable $\bar{x}_4^\mu=(q_i\bar{x}_l^\mu)+t$ and they can be written by their Fourier series. For a commensurate modulation, only a finite number of $u_l^\mu(\bar{x}_4^\mu)$ values are real displacements in the modulated structure. This number is the order of the superstructure. In our case, this order is 2 and the Fourier series can be restricted to the first order without any approximation:

$$u_l^\mu(\bar{x}_4^\mu)=A_l^\mu\cos2\pi\bar{x}_4^\mu+B_l^\mu\sin2\pi\bar{x}_4^\mu\ . \tag{9}$$

The basic structure, which is characterized by the

TABLE II. Symmetry elements of the superspace group $P^{Amma}_{1\,\bar{1}\,s}$ with the cell origin at $t=\frac{1}{8}$.

1	$(E,1/0,0,0,0)$	5	$(I,1/0,0,0,\frac{3}{4})$
2	$(m_x,1/\frac{1}{2},0,0,0)$	6	$(2_x,1/\frac{1}{2},0,0,\frac{3}{4})$
3	$(2_y,1/0,0,0,\frac{1}{2})$	7	$(m_y,1/0,0,0,\frac{1}{4})$
4	$(m_z,1/\frac{1}{2},0,0,\frac{1}{2})$	8	$(2_z,1/\frac{1}{2},0,0,\frac{1}{4})$

average-position parameters, is the structure of phase II. There are five independent atoms, respectively, in special positions *a*, *b*, *c*, and *f* for Fe, F(1), K and F(2), and (F3). There are four independent average-position parameters ($\bar{x}_i^{\mu}$). The fact that the atoms are in special positions also implies restrictions for the displacements: the displacement of an atom which is changed into itself by a symmetry operation has to be invariant by this operation, i.e.,

$$u_i^{\mu}(\bar{x}_4^{\mu}) = \sum_{j=1}^{3} R_{ij} u_j^{\mu}(\epsilon(\bar{x}_4^{\mu} - \tau)), \quad i = 1,2,3 , \tag{10}$$

where R_{ij} is the matrix element of the symmetry operator and τ is the fourth coordinate of its associated translation.

Using this relation and the preceding development of the displacement of each independent atom, one obtains 11 independent positional parameters for the Fourier amplitudes A_i^{μ} and B_i^{μ}. The modulated structure is then described by 15 positional parameters and, respectively, 5 and 16 independent parameters for the isotropic and anisotropic temperature factors.

The program REMOS (Ref. 18) calculated the structure factors using the preceding four-dimensional analysis and minimized the reliability factor R_w:

$$R_w = \sum_i w_i (F_i^{\text{obs}} - F_i^{\text{calc}})^2 \Big/ \sum_i w_i F_i^{\text{obs2}} , \tag{11}$$

where w_i is a weight factor, and F_i^{obs} and F_i^{calc} are the observed and calculated structure factors. Unit weights have been used for all reflections. The atomic-scattering factors have been taken from Ref. 19. After correction of secondary extinction, the refinement converged at $R_w = 0.046$ for 1410 reflections. Final parameters are listed in Table III.

This R factor is quite equivalent to 3D R factors ($R = 0.047$ and $R = 0.044$, respectively, with unit weights and nonunit weights in space group *Pmcn*) but the number of refinement parameters is reduced in the 4D refinement from 60 to 31. By averaging the final values of

TABLE III. Final-position and thermal parameters. Italic numbers represent the allowed parameters of the 4D refinement. Numbers in square brackets are the values calculated from the equivalent final parameters of the 3D refinement (Ref. 9).

		Average	*A*	*B*	B_{eq}
K	*x*	0.25	0.0	0.0	*1.41(2)*
		[0.25]	[0.0]	(0.0)	[1.40][a]
	y	0.0	*0.0007(3)*	*−0.0007(3)*	
		[0.0]	[0.0][a]	[0.0][a]	
	z	*0.729 32(7)*	*−0.0039(1)*	*−0.0039(1)*	
		[0.729 23]	[−0.0037]	[−0.0037]	
Fe	*x*	0.0	*0.0005(1)*	*0.0005(1)*	*0.533(3)*
		[0.0]	[0.0004]	[0.0004]	[0.606]
	y	0.0	0.0	0.0	
		[0.001][b]	[0.0]	[0.0]	
	z	0.0	*−0.0011(1)*	*−0.0011(1)*	
		[0.0]	[−0.0011]	[−0.0011]	
F(1)	*x*	0.0	*0.0316(4)*	*0.0316(4)*	*1.69(3)*
		[0.0]	[0.0313]	[0.0313]	[1.75]
	y	0.0	0.0	0.0	
		[−0.0046][b]	[0.0]	[0.0]	
	z	0.5	*0.0016(3)*	*0.0016(3)*	
		[0.5]	[0.0017]	[0.0017]	
F(2)	*x*	0.25	0.0	0.0	*1.25(6)*
		[0.25]	[0.0]	[0.0]	[1.31][a]
	y	0.0	*−0.0581(7)*	*0.0581(7)*	
		[0.0]	[−0.0581][a]	(0.0581)[a]	
	z	*−0.0341(3)*	*−0.0015(4)*	*−0.0015(4)*	
		[−0.0341]	[−0.0014]	[−0.0014]	
F(3)	*x*	*0.0466(3)*	*0.0010(4)*	*0.0010(4)*	*1.34(4)*
		[0.0467]	[0.0010]	[0.0010]	[1.39][a]
	y	0.0	*−0.0112(7)*	*0.0112(7)*	
		[0.0]	[−0.0106][a]	[0.0106][a]	
	z	*0.1495(2)*	*−0.0014(2)*	*−0.0014(2)*	
		[0.1493]	[−0.0010]	[−0.0010]	

[a]Average value of two different independent parameters.
[b]Value fixed to 0 by symmetry.

equivalent independent refinement positional and thermal parameters of the 3D study,[9] it is possible to calculate the corresponding parameters of the 4D description. These values are given in square brackets in Table III; they are very close to the refined values of the 4D study. The number of reflections is not exactly the same in both refinements because some very weak intensities at the vanished nodes of the basic structure, allowed in the *Pmcn* space group, have been suppressed in the second refinement. Either they are second-order satellites ($m=\pm 2$) or they have not been correctly measured.

The interatomic distances have been calculated with the final values of the 4D description. Their typical values for an octahedron FeF_6 are given in Table IV. They are about the same as in the first study, except the Fe-F(1) distances. In the superstructure description (*Pmcn*), there are two nonequivalent distances in an octahedron: 1.946(4) Å and 1.973(4) Å.[20] In the 4D description, these two distances are still nonequivalent but their refined values are identical within their standard deviations: 1.9596(40) Å and 1.9603(40) Å. The Fe atoms do not seem to move along the Fe—F(1) bonding. The F-F distances are almost the same in phases II and III, and the distortion of the octahedra during the phase transition is very small. The structural evolution during this transition II→III corresponds to a tilt of the octahedra of about 7.0(2)° around the **c** axis, as already discovered in our first study.[9]

Thus, the 4D refinement in space group $P\,{}^{Amma}_{1\,\bar{1}\,s}$ confirms very clearly the previous structural result in space group *Pmcn*, and gives an equivalent structural description. But it allows us to give a better description of the symmetry, taking into account all the extinction conditions of the diffraction pattern, and consequently, it allows us to reduce the number of independent refinement parameters.

IV. LANDAU THEORY, ORDER PARAMETER, AND SUPERSPACE GROUP

After the structural description of the modulated structure, we are now going to describe the symmetry of the low-temperature phase by means of the irreducible representations (IR's) of the space group of phase II, considered as the prototype high-temperature phase. In the first part, we shall consider the Landau theory for continuous structural transitions[21,22] and derive the active IR's leading to phase II. In the second part, we shall derive the symmetry operations of the modulated structure from the preceding IR's, following the analysis proposed by Perez-Mato *et al.*[23,24]

The transition is associated with the wave vector **q** $(0,\frac{1}{2},0)$ and so, we must consider the IR's of the space group *Amma* at the point $(0,\pi/b,0)$ of the Δ line of the Brillouin zone. Let Γ_1, Γ_2, Γ_3, and Γ_4 be these four two-dimensional IR's. They are given in Table V.[25] The components of the order parameter associated with a two-dimensional IR Γ_i are Q and its complex conjugate Q^* ($Q=\rho e^{i\varphi}$ and $Q^*=\rho e^{-i\varphi}$).

Let us now consider the symmetry operations for each IR that leave the components of the order parameter invariant, and the conditions on the phase value φ necessary to realize this invariance property. This phase value φ will only have an influence on the mirror plane orthogonal to **b**. If $\varphi=0 \bmod(\pi/2)$, the mirror m_y is present in phase III, while if $\varphi=\pi/4 \bmod(\pi/2)$, the mirror is associated with a translation of **c**/2. In the other cases, the mirror plane is lost.

One can deduce from the present analysis the different 3D space groups associated with each IR Γ_i and with each value of the phase φ. They are given in Table VI. Each IR gives two centrosymmetric space groups for the particular values of $\varphi=0 \bmod(\pi/4)$ and a noncentrosymmetric one for the other values of φ.

After these preliminary symmetry considerations, it is now possible to determine the stable solutions, i.e., the solutions which minimize the free energy F. The expansion of the density of F can be written

$$F(Q,Q^*)=\alpha QQ^*+\beta(QQ^*)^2+\gamma(Q^4+Q^{*4}) +i\sigma\left[Q\frac{\partial Q^*}{\partial y}-Q^*\frac{\partial Q}{\partial y}\right]+\chi\left[\frac{\partial Q}{\partial y}\frac{\partial Q^*}{\partial y}\right]. \tag{12}$$

The fourth term is a Lifchitz invariant. The existence of such a term in the free-energy expansion claims either that the transition is really discontinuous or that the low-temperature phase is inhomogeneous.[26] Therefore, an intermediate incommensurate phase between phases II

TABLE IV. Interatomic (Fe-F) and (F-F) distances (Å) and cell parameters in phases II and III. Standard deviations are given in parentheses.

	Phase II	Phase III			
a	7.645(1)	7.612(1)			
b	3.906(1)	3.890(1)			
c	12.323(2)	12.297(2)			
Fe-F(1)	1.953(1)	1.960(4)	1.960(4)		
Fe-F(2)	1.957(2)	1.959(3)	1.964(3)		
Fe-F(3)	1.868(2)	1.870(3)	1.876(3)		
F(1)-F(2)	2.765(3)	2.772(4)	2.779(4)	2.774(4)	2.767(4)
F(1)-F(3)	2.702(3)	2.686(4)	2.709(4)	2.735(4)	2.714(4)
F(2)-F(3)	2.740(3)	2.740(4)	2.747(4)		

TABLE V. Irreducible representations of $D_{2k}^{17} = Amma$ at $(0,\pi/b,0)$.

D_{2h}^{17}	Γ_1	Γ_2	Γ_3	Γ_4
1 Id	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$
2 m_x	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$
3 2_y	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$
4 m_z	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$
5 I	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$
6 2_x	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$
7 m_y	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$
8 2_z	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$
$A(0,\frac{1}{2},\frac{1}{2})$	$\begin{bmatrix}i&0\\0&\bar{i}\end{bmatrix}$	$\begin{bmatrix}i&0\\0&\bar{i}\end{bmatrix}$	$\begin{bmatrix}i&0\\0&\bar{i}\end{bmatrix}$	$\begin{bmatrix}i&0\\0&\bar{i}\end{bmatrix}$

and III could exist.[7,11] In the last hypothesis, the transition between the intermediate phase and phase III should be a lock-in transition, which is usually a first-order one, but the discontinuity can be very weak. This hypothesis seems to agree with Saint-Grégoire's study[11] and with our previous results (Sec. II).

The stability conditions are the same for all the IR's

$$\varphi = 0 \bmod(\pi/4) . \tag{13}$$

In a preceding study,[11] only the case $\varphi=0$ had been considered and we have seen from Table VI that it leads to the space group *Pmmn* for the IR Γ_4. This last space group is also proposed by Hidaka.[6] But now we must also consider the possible solution $\varphi=\pi/4$, and in the same IR Γ_4 this value leads to the space group *Pmcn*, which agrees with our preceding structural determination.[9]

In any case, the symmetry of the order parameter is given by the IR Γ_4 and it is now possible to make a comparison between these last results and the 4D analysis of Sec. III. The four IR's of the space group *Amma* at the point $(0,\pi/b,0)$ can be associated with the four possible superspace groups with basic structure *Amma*, and the different choices of the phase value of the order parameter can be associated with the different sections of the superspace groups by the physical space; the phase φ value of the order parameter is equivalent to the phase variable t of the 4D treatment. The equivalence is outlined in

TABLE VI. 3D-space groups related to each IR of D_{2h}^{17} and to the different possible values of the phase φ of the order parameter, and 3D-space groups related to the different possible sections of the different superspace groups of basic structure *Amma*.

Phase φ / IR	$\varphi=0 \bmod(\pi/2)$	$\varphi=(\pi/4) \bmod(\pi/2)$	$\varphi\neq 0 \bmod(\pi/4)$	
Γ_1	*Pmma*	*Pmca*	*Pm2a*	$P^{Amma}_{1\,\bar{1}\,1}$
Γ_2	*Pbma*	*Pbca*	$Pb2_1a$	$P^{Amma}_{s\,\bar{1}\,1}$
Γ_3	*Pbmn*	*Pbcn*	*Pb2n*	$P^{Amma}_{s\,\bar{1}\,s}$
Γ_4	*Pmmn*	*Pmcn*	$Pm2_1n$	$P^{Amma}_{1\,\bar{1}\,s}$
	$t=0 \bmod(\frac{1}{4})$	$t=\frac{1}{8} \bmod(\frac{1}{4})$	$t\neq 0 \bmod(\frac{1}{8})$	Section / Superspace group

Table VI where one can see the different 3D space groups associated either with an IR Γ_i and a φ value, or with a superspace group and a t value.

Up until now we have clarified the symmetry of the low-temperature phase III, first using the crystallographic concepts of the four-dimensional superspace groups on the basis of the description of the diffraction pattern, and second using the Landau theory. Both descriptions are not independent. It is possible to find again the superspace group or the equivalent symmetry operations straight from the IR Γ_4. For an incommensurate structure which results from the appearance of a displacive distortive mode at the transition, it has been shown that the superspace group can be deduced from an enlarged group of transformation which leaves the Landau free-energy expansion invariant.[23,24]

The normal coordinates of the distortive mode of the low-temperature phase, belonging to the IR Γ_4, are $\{Q,Q^*\}$, and these coordinates transform into $\{Q',Q'^*\}$ by the action of the symmetry operator $(R/\mathbf{v})$:

$$\begin{bmatrix} Q' \\ Q'^* \end{bmatrix} = D_4(R/\mathbf{v}) \begin{bmatrix} Q \\ Q^* \end{bmatrix}, \tag{14}$$

where $D_4(R/\mathbf{v})$ is the matrix of the IR Γ_4 corresponding to the symmetry operator $(R/\mathbf{v})$. We can easily verify that the Landau expansion (12) is invariant through the action of the symmetry operations of the group $G_0 = Amma$.

In particular, it must be invariant through all the translation operations of this group. If the modulation vector $\mathbf{q}$ were incommensurate, such a translation operation would correspond to an irrational phase translation of the normal coordinates. This would induce the invariance of F through any arbitrary phase translation of the normal coordinates, and this would imply that γ in (12) should be 0. In fact, $\mathbf{q}$ is commensurate ($\mathbf{q}=\frac{1}{2}\mathbf{b}^*$) and all the translation operations of G_0 are only associated with a finite number of phase translations $(0,\pi/2,\pi,3\pi/2)$ modulo 2π and one can then easily verify the effective invariance of F.

In the case of an incommensurate phase, Perez-Mato has still shown that it is possible to consider more general transformations keeping the free-energy invariant, which consist by associating to a symmetry operation $(R/\mathbf{v})$ of G_0, a phase translation ϕ of the normal coordinates $\{Q,Q^*\}$, in such a way that we can write

$$\begin{bmatrix} Q' \\ Q'^* \end{bmatrix} = \begin{bmatrix} \exp(2\pi i\phi) & 0 \\ 0 & \exp(-2\pi i\phi) \end{bmatrix} D_4(R/\mathbf{v}) \begin{bmatrix} Q \\ Q^* \end{bmatrix}. \tag{15}$$

In this case, this is a consequence of the invariance of F through the action of any arbitrary translation of the coordinate phases. The set of these generalized transformations forms a group. The superspace group corresponds to the subgroup of this general group which keeps the modulated structure invariant, i.e., which leaves the normal coordinates unchanged.

In our commensurate case, most of the terms of the free-energy expansion are effectively invariant through such an operation, except for the third term $\gamma(Q^4+Q^{*4})$. If we consider only the pure phase translations

$$\begin{bmatrix} Q' \\ Q'^* \end{bmatrix} = \begin{bmatrix} \exp(2\pi i\phi) & 0 \\ 0 & \exp(-2\pi i\phi) \end{bmatrix} \begin{bmatrix} Q \\ Q^* \end{bmatrix}. \tag{16}$$

The invariance of this third term implies the particular values $\{0,\frac{1}{4},\frac{1}{2},\frac{3}{4}\}$ modulo $\mathbb{Z}$ of ϕ, and we have seen that this choice is related to the commensurability of the $\mathbf{q}$ vector. The only difference with the incommensurate case is that now the set of the phase translations forms a discrete group.

The symmetry group of the low-temperature phase is given by all the symmetry operations $(R_j/\mathbf{v}_j)$ and the associated phase translation ϕ_j, keeping the normal coordinates of the order parameter invariant:

$$\begin{bmatrix} Q \\ Q^* \end{bmatrix} = \begin{bmatrix} \exp(2\pi i\phi_j) & 0 \\ 0 & \exp(-2\pi i\phi_j) \end{bmatrix} D_4(R_j/\mathbf{v}_j) \begin{bmatrix} Q \\ Q^* \end{bmatrix}. \tag{17}$$

First, let us consider the case $(R_j = Id, \mathbf{v}=\mathbf{0})$. Relation (17) implies $\phi_j = 0 \bmod(\mathbb{Z})$. So we can associate with the identity in R^3, the enlarged symmetry operations $[Id/(0,0,0);n]$ $(n\in\mathbb{Z})$. These operations are equivalent to the pure translation operations along the fourth direction of our superspace symmetry group. In the following, all the ϕ values will be given modulo $\mathbb{Z}$.

In the same way, the basic R^3 translations $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ become, respectively, $[Id/(1,0,0);0]$, $[Id/(0,1,0);-\frac{1}{2}]$, and $[Id/(0,0,1);0]$ which are, respectively, equivalent to the translations $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ of the supercrystal. The centering translation $(\mathbf{b}/2+\mathbf{c}/2)$ becomes $[Id/(0,\frac{1}{2},\frac{1}{2});\frac{3}{4}]$ which corresponds to a pure centering translation of our 4D cell (the lattice translation $(\mathbf{a}_2/2+\mathbf{a}_3/2)$ corresponding to the A centering in the 4D cell is equivalent from (6) to the translation $(\mathbf{b}/2-\mathbf{e}_4/4+\mathbf{c}/2)$ which is directly described by the notation $[Id/(0,\frac{1}{2},\frac{1}{2});\frac{3}{4}]$).

One can also deduce the ϕ value attached to each symmetry operator of G_0: these respective values for the operations $[Id/(0,0,0)]$, $[m_x/(\frac{1}{2},0,0)]$, $[2_y/(0,0,0)]$, and $[m_z/(\frac{1}{2},0,0)]$ are 0, 0, $\frac{1}{2}$, and $\frac{1}{2}$. They correspond to the respective associated translations in the fourth direction for the corresponding 4D symmetry operators of Table II.

For the other symmetry operations of G_0 which inverse $\mathbf{q}$ into $-\mathbf{q}$, the relation (17) gives a condition which depends on the phase φ of the order parameter. As a matter of fact, the choice of this phase φ is related to the choice of the origin along the internal direction of the supercrystal, and the phase translation associated with such a symmetry operation which reverses $\mathbf{e}_4$, depends on the choice of the origin along this axis. Considering, for example, the inversion operation, from (17), one can write

$$\begin{bmatrix} Q \\ Q^* \end{bmatrix} = \begin{bmatrix} \exp(2\pi i\phi_j) & 0 \\ 0 & \exp(-2\pi i\phi_j) \end{bmatrix} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} Q \\ Q^* \end{bmatrix} \tag{18}$$

with $Q=\rho e^{i\varphi}$. It follows: $\phi_j=\varphi/\pi \bmod(\mathbb{Z})$.

We have seen that ϕ_j must be 0, $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ modulo $\mathbb{Z}$, which implies particular values for φ. These values correspond to the stability conditions (13) derived from the minimizing of the Landau free-energy expansion.

Taking $\varphi=0$, the inversion becomes $[I/(0,0,0);0]$ and the related group in the 3D space is *Pmmn*. Taking $\varphi=3\pi/4$, the inversion becomes $[I/(0,0,0),\frac{3}{4}]$, which corresponds to the symmetry element 5 in Table II. The related 3D space group is *Pmcn* and corresponds to the section $t=\frac{1}{8}$ of our 4D solution $P\,{}^{Amma}_{1\,\bar{1}\,s}$. So a change of the φ value corresponds to a translation of the origin along the fourth axis. This approach allows us to find again the superspace group and the stability conditions.

V. DISCUSSION AND CONCLUSION

In the present work we have confirmed our previous results about the structure of phase III of $KFeF_4$ by considering this phase as a modulated one, by the two different approaches usually used for the structural description of the incommensurate modulated structures: on the one hand, the 4D analysis in the superspace group symmetry (Sec. III), on the other hand, the symmetry analysis by means of the free-energy expansion and of the theory of the IR's (Sec. IV). These methods are also adequate to describe the commensurate modulated structures, even of lower order, and have been proved to give consistent descriptions. They allow us to give a better interpretation of the diffraction pattern and to describe the whole symmetry of the modulated phase, which is only partially given by a classical 3D-space group, and thus, to need a smaller number of refinement parameters. The 4D description is more rapidly deduced from the observation of the diffraction pattern and the tabulation of the monoincommensurate 4D-space groups, and it offers more facilities to derive the final structural parameters. The second description, based on the invariance of the free energy, outlines the IR which governs the atomic displacements, during the phase transition II→III. It allows us to derive together the group of the generalized symmetry operations equivalent to our superspace group, the particular value of the phase φ equivalent to our particular sections, and to give the stability conditions of the modulated structure.

A further analysis of the atomic displacements in the modulated structure shows that they are compatible with a rotation of all the octahedra FeF_6 around the **c** axis (displacements $u_1^{F(1)}$, $u_2^{F(2)}$, and $u_2^{F(3)}$), associated with a deformation (displacements $\mathbf{u}^{Fe}$, $u_3^{F(1)}$, $u_3^{F(2)}$, and $u_3^{F(3)}$) and with a displacement of the K atoms in the **b**-**c** plane (displacements u_2^{K} and u_3^{K}). From the final parameters of the refinement (Sec. III, Table III), one can see that the amplitudes of the parameters of the first group are higher than the amplitudes of the other groups and, in fact, the combination of all the real atomic displacements almost reduce to a rigid-body rotation of the octahedra around the **c** axis.

If we reduce the mechanism of the transition in this way, we can identify the angle ω of the rotation of the octahedra to be a good approximation of the amplitude of the order parameter of the transition. A rough estimation of this parameter can be done from the evolution of the lattice parameters as a function of the temperature, as it was derived from powder dilatometric curves (Sec. II). In phase II, we have observed a linear variation of the *a* and *b* parameters and in this range of temperature, we can agree that the *b* parameter is twice the Fe-F(1) interatomic distance, because the atoms are aligned along the *b* direction, regardless to the anisotropic thermal motion of F atoms along the *a* direction.

The observed contraction of the *b* parameter at the transition corresponds to the tilt of the octahedra, and the new *b* parameter should now be given by

$$B_{III}=2d[\mathrm{Fe}-\mathrm{F}(1)]\cos\omega \ . \tag{19}$$

A quantitative determination of the ω parameter from this relation is not reliable, since it would require an accurate knowledge of the interatomic distances Fe-F(1) as a function of the temperature; nevertheless, the relative evolution of the *b* parameter is well compatible with a similar evolution of an order parameter associated with the transition II→III and this confirms the interpretation of phase III as modulated structure of phase II.

Thus, $KFeF_4$ is a good example which proves that the 4D analysis also very adequate to deal with some superstructures which can be interpreted as modulated structures. In the same family, $KAlF_4$ (Refs. 27 and 28) has a structure which is very close to the structure of $KFeF_4$. This compound presents a phase transition at 250 K; although the mechanism of the transition is very different (it is a martensitic one), these two structures can be described from the same prototype structure: the structure of phase II of $KFeF_4$ (Fig. 2). As phase III of $KFeF_4$, the low-temperature phase of $KAlF_4$ is derived from the basic structure by a tilt of the octahedra around the **c** axis (about 4°) which imposes the doubling of the *b* pa-

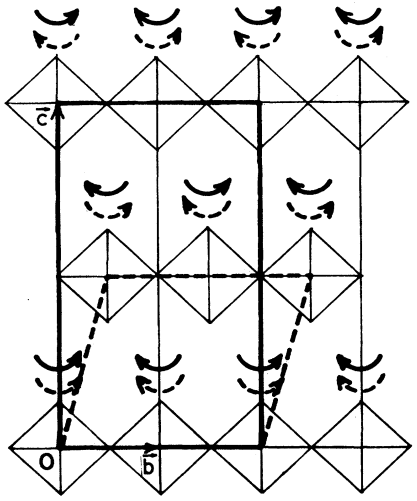

FIG. 6. Schematic representation of the tilt of the octahedra layers in $KFeF_4$ (solid lines, cell **a**,2**b**,**c**, space group *Pmcn*) and $KAlF_4$ (dotted lines, cell **a**,2**b**,(**c**-**b**)/2, space group $P2_1/m$).

rameter (the *a* parameter in the setting chosen by Launay *et al.*[27]). But the symmetry relations between two adjacent octahedra layers are different as it is shown in Fig. 6, and lead to two different lattices for the low-temperature phases: the **c** translation is kept for $KFeF_4$, but not the *A* centering and conversely for $KAlF_4$; this leads, respectively, to an orthorhombic and to a monoclinic lattice. This can be also seen from the diffraction patterns, which are similar to the main reflections and differ by the positions of the superstructure reflections; for $KAlF_4$ they are located at $(0,\frac{1}{2},\frac{1}{2})$ and $(0,-\frac{1}{2},-\frac{1}{2})$ from the main reflections and all systematic extinctions are in agreement with the 3D-space group $P2_1/m$. There is no extra extinction rule which cannot be explained by a symmetry operation of a 3D-space group.

Thus, the treatment of the low-temperature phase of $KAlF_4$, by the previous methods for modulated structures would not give a better description of the structure, and both descriptions in 3D and 4D analysis should be equivalent. But, in the same family, the compounds KVF_4 and $KTiF_4$ are isostructural with $KFeF_4$, and we can make the assumption that they could be usefully described as modulated structures, even if they are characterized by a first-order transition.

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*Present address: Laboratoire de Chimie Appliquée, Université de Genève–Science II, CH-1211 Genève 4, Switzerland.

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