

# The Electron Microscopic Observation of Phase Transitions in $\text{KFeF}_4$ , $\text{RbFeF}_4$ , and $\text{RbVF}_4$ <sup>1</sup>

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Electron diffraction experiments reveal a novel phase transition in  $\text{RbFeF}_4$  and confirm the existence of phase transitions at 368 K in  $\text{KFeF}_4$ , at 378 K in  $\text{RbFeF}_4$ , and at 413 K in  $\text{RbVF}_4$ . At variance with other studies it is found that the periodicity along the  $c$  axis is doubled in the room temperature phase of  $\text{RbFeF}_4$  and there is no indication for the disappearance of this doubling at 413 K in  $\text{RbVF}_4$ . A proposal for the structural characteristics of the phases involved in this transition is made, using the complete list of possible structures obtained when only tilting of rigid octahedra is allowed. Some attention is also paid to decomposition phenomena under electron irradiation. © 1985 Academic Press, Inc.

## 1. Introduction

A number of  $ABX_3$  (perovskite) compounds such as  $\text{CaTiO}_3$  and  $\text{NaNbO}_3$  undergo phase transitions featuring the condensation of soft phonon modes upon lowering the temperature (1).

These condensed modes must have symmetries belonging to a space group which is a subgroup of the space group of the high temperature structure. The structure with highest symmetry is often called the "aristotype" whereas the structures derived from it by a symmetry reduction are called "hettotypes." This nomenclature was first introduced by Megaw (2). Glazer (3) pointed out that the most important symmetry reduction during these transitions results from the tilting of rigid  $BX_6$  octahe-

dra since the low frequency phonons involved do not deform the octahedra. A general tilting scheme can always be decomposed in tilt components around the three octahedral tetrad axes.

Glazer proposed a classification of all the possible  $ABX_3$  hettotypes based on the fact that the magnitude of tilting of one octahedron around each of the "pseudocubic" axes, connecting the  $B$  cations at right angles, combined with the correlation between the senses of tilting of the octahedra along these axes, fully determines the structure if no periodicities larger than two arise and generally they do not.

The  $ABX_4$  compounds are structurally related with the perovskites because they are also built up by  $BX_6$  octahedra; however, they are no longer vertex-sharing in the third dimension as can be seen from Fig. 1b. In spite of this structural difference phase transitions involving tilting octahedra do also occur in  $ABX_4$  materials (4-9) and

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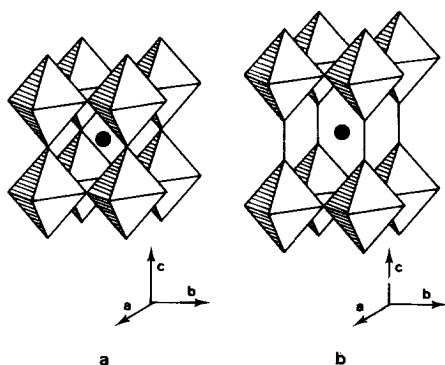


Fig. 1. (a) Aristotype structure ( $Pm\bar{3}m$ ) of the  $ABX_3$  compounds ( $A, B = \text{cation}, X = \text{anion}$ ). The anions form the vertices of the  $BX_6$  octahedra, whereas the  $A$  cation is indicated as a black circle. (b) Aristotype structure ( $P4/m\bar{m}m$ ) of the  $ABX_4$  compounds. It is clearly seen that the  $BX_6$  octahedra are no longer vertex-sharing along  $c$ .

as a consequence Glazer's classification is extensively used for the description of the  $ABX_4$  hettotype structures.

It is, however, quite clear that due to the loss of mechanical constraints in the  $ABX_4$  case more hettotypes are possible, and as a consequence the  $ABX_3$  classification must be degenerate.

Bulou (9) therefore suggests to extend the symbol proposed by Glazer, with two subscripts, so as to account for the supplementary degrees of freedom. The general extended symbol then becomes

$$a_u^i b_v^j c^k$$

where  $a, b,$  and  $c$  indicate that the tilt magnitude around each axis is different. Equal tilts around two axes result in the repetition of the same letter.

The superscripts  $i, j,$  and  $k$  can be either  $+, -,$  or  $0$  depending on the tilt correlation.

If the tilt correlation is positive alternate octahedra along the considered axis have the same sense of tilting whereas negative tilt correlation means that alternate octahedra are tilted in the opposite sense. Zero tilt correlation clearly indicates that no tilt at all is present along the considered axis.

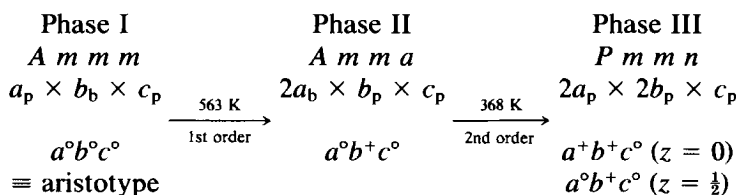
It is clear that tilting around an axis will double the periodicity along the perpendicular axis if the octahedra along that axis are vertex-linked whereas negative tilt correlation will also double the periodicity along the considered axis.

The subscripts  $u$  and  $v$  are added to account for the loss of mechanical constraints. Indeed, along the  $c$  axis successive octahedra may be tilted either parallel ( $p$ ) or antiparallel ( $a$ ) around the  $a$  and the  $b$  axes (which is not the case for perovskites where it is always antiparallel due to the vertex linking along the  $c$  axis. So  $u$  and  $v$  can be either "a" or "p."

$KFeF_4$  has an aristotype structure which is somewhat different from the structure shown in Fig. 1b (4).

Alternate layers of vertex-sharing octahedra are shifted over  $1/2\bar{b}_p$ , where  $|\bar{b}_p|$  is the shortest distance between two octahedra along the  $b$  axis. The subscript  $p$  means "pseudotetragonal" to indicate that the translation has to be taken along the line connecting the  $B$  cations, i.e., along the former tetragonal  $b$  axis.

By means of X-ray diffraction and dielectric constant measurements Hidaka *et al.* (5) found two transitions: one of second order at 368 K and one of first order at 563 K. The structural features of the phases involved are given below:

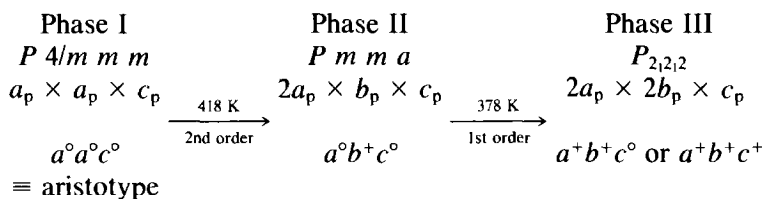


$RbFeF_4$  and  $RbVF_4$  have an aristotype as shown in Fig. 1b and both compounds were recently investigated by Hidaka *et al.* (7, 8).

X-Ray diffraction, dielectric constant measurements, optical observations, and

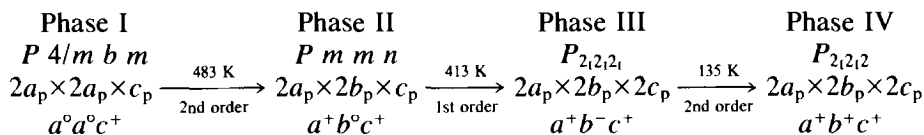
specific heat measurements show that  $RbFeF_4$  undergoes a first-order transition at 378 K and a second-order transition at 418 K (7).

The characteristic features are represented below:



$RbVF_4$  on the contrary undergoes three transitions at, respectively, 135, 413, and 482 K. The transition at 413 K is reported

as first-order whereas the others are second-order transitions (8). They can be represented as follows:



Note that the extended symbol is not used here and some ambiguity about the real structure still remains.

For the sake of simplicity all indices are referred to a superstructure cell with lattice parameters  $2a_p$ ,  $2b_p$ , and  $2c_p$ . The letter "u" (*ungerade*) will indicate an odd index, whereas the letter "g" (*gerade*) will indicate an even index. Reflections with at least one index "u" are therefore superstructure reflections.

It is then useful to indicate various types of reflections using the following Brillouin zone notation:

$$\begin{array}{ll}
 F = g g g & A = u u u \\
 X = u g g & R = u g u \\
 Y = g u g & S = g u u \\
 Z = g g u & M = u u g
 \end{array}$$

whereby  $F$  are the basic structure reflections and  $X$ ,  $Y$ ,  $Z$ ,  $A$ ,  $R$ ,  $S$ , and  $M$  are super-

structure reflections, as can be seen in Fig. 2.

This notation provides a powerful shorthand notation representing schematically what happens in reciprocal space in the course of a transition by simply stating which superstructure reflections are present for a particular phase.

This code will be called henceforth the "diffraction typology." For example, the phase with structure

$$a_a^+ a_p^- c^+ \quad (P 2/m)$$

has a diffraction typology  $RSM$ .

## 2. Experimental

Because the investigated materials are layered compounds, with pronounced cleavage, the normal to the layers being parallel with the  $c$  axis, the samples for

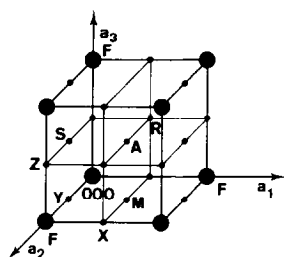


FIG. 2. Schematic representation of the types of reflections in the Brillouin zone notation.

electron microscopic investigation were thinned by stripping off layers from a plate-like crystal of  $(2 \times 2 \times 0.5) \text{ mm}^3$  using splice tape. Due to this pronounced preferential cleavage the samples have a plate shape such that most observations have to be performed close to a zone axis parallel to  $[001]$ .

After washing in benzene, in order to remove tape residues, the thinned plates are mounted on 3-mm copper grids by means of silver paste to ensure good thermal and electrical contact.

In spite of these precautions electrical conduction remains a problem and substantial charging phenomena still occur under the electron bombardment for observation. Moreover, all materials are subject to damage by electron irradiation.

## 2.1. Phase Transitions

The transitions are observed in the electron diffraction mode. When heating, the temperature is controlled by means of a thermocouple in contact with the specimen furnace inside the microscope. However, due to heating caused by electron irradiation, the temperature in the area under examination is somewhat higher than the furnace equilibrium temperature. Cooling is performed with a specimen holder allowing to cool down to liquid nitrogen temperature (LNT).

A preliminary report of the experimental results was communicated at the XIII Congress of Crystallography (11).

### 2.1.1. $K\text{FeF}_4$

The phase transition at 368 K is observed in a zeroth order  $[001]$  zone pattern as shown in Fig. 3 and confirms the result of Hidaka. The cluster of reflections surrounding each basic structure reflection should be ignored because it is associated with the decomposition process under electron irradiation.

The distribution of the intensity within each cluster indicates that convolution of two lattices must be considered.

The presence of periodic antiphase

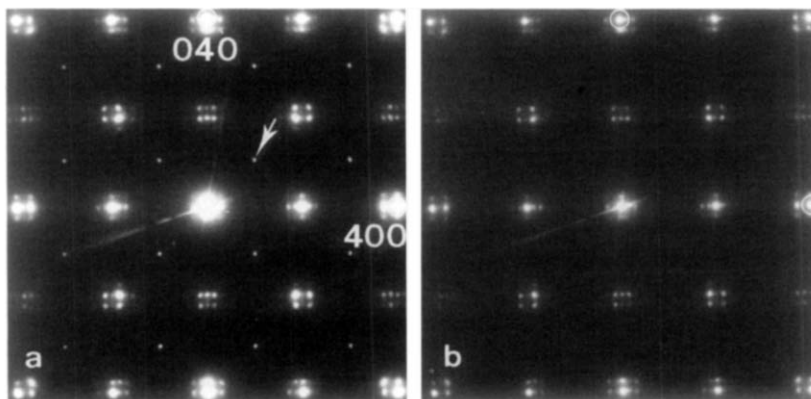


FIG. 3. Phase transition at 368 K as observed in the  $[001]$  zone diffraction pattern of  $K\text{FeF}_4$ . In this projection the transition is seen as the disappearance of the  $M$  type reflections as indicated.

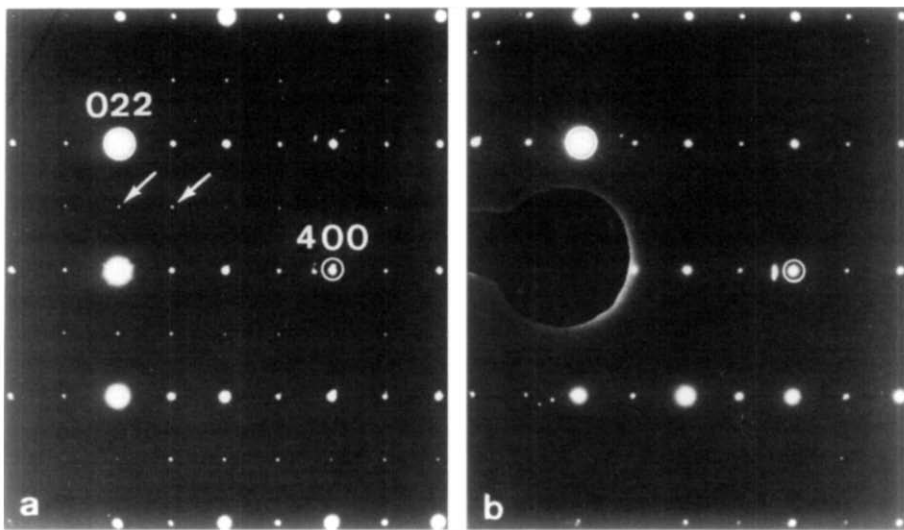


FIG. 4. Phase transition in  $\text{RbFeF}_4$  when cooling down to LNT as observed in a  $[01\bar{1}]$  zone diffraction pattern. (a) The RT phase clearly shows reflections of the type  $(hk u)$  as indicated by arrows. (b) The LNT phase.

boundaries along which the octahedra become edge-sharing can be proposed as an initial stage of the decomposition.

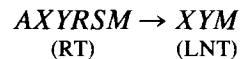
### 2.1.2. $\text{RbFeF}_4$

The transition at 378 K is observed with electron diffraction techniques in the zeroth order  $[011]$  zone pattern. No diffuse intensity is found, which excludes the presence of possible short range order.

Reflections of the type  $(u g 0)$  and  $(g u 0)$  present in the room temperature (RT) phase, disappear with increasing temperature whereas reflections of the type “ $u u 0$ ” do not. The second phase transition at 418 K was not observed although the samples were heated up to the decomposition temperature.

Hidaka *et al.* (7) did not mention any doubling of the periodicity along the  $c$  axis but  $[011]$  and  $[0\bar{1}1]$  zone axis patterns clearly show reflections of type  $(hk u)$  at RT as can be seen in Fig. 4a. Upon cooling to LNT these reflections disappear as shown in Fig. 4b. All observed changes in reciprocal space concomitant with the tran-

sition can be represented using the shorthand notation which is explained in the introduction:



Finally Fig. 5 visualizes the changes in reciprocal space schematically.

### 2.1.3. $\text{RbVF}_4$

The transition at 413 K is observed in a  $[001]$  zone pattern and involves the disappearance of the  $(u g 0)$  and the  $(g u 0)$  reflections which can be seen in Fig. 6 and

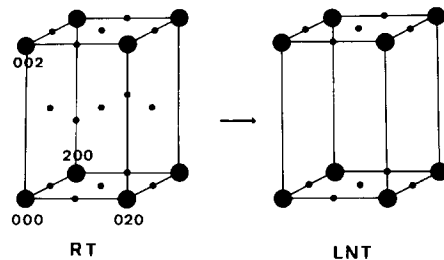


FIG. 5. Schematic representation of the phase transition between RT and LNT as observed in  $\text{RbFeF}_4$ .

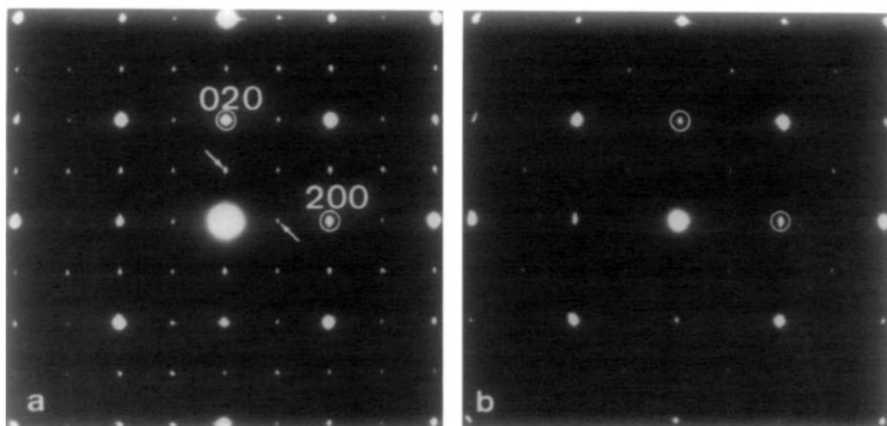


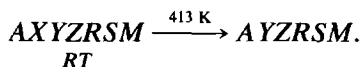
FIG. 6. Phase transitions at 413 K as observed in the [001] zone diffraction pattern of  $\text{RbVF}_4$ . Projected along this axis the transition is revealed by vanishing  $X$  and  $Y$  reflections.

which is equivalent with what is observed in  $\text{RbFeF}_4$ . Heating up to 720 K shows no evidence for other transitions as revealed in this projection of reciprocal space.

At temperatures above the first transition, careful investigation of reflections belonging to higher-order [001] zones indicates that the doubling of the periodicity along the  $b$  axis also disappears.

There is, however, no indication for the extinction of reflections of type  $(h k u)$  as reported by Hidaka *et al.* (8).

In summary, the changes in the diffraction patterns occurring at the transition at 413 K read



In Fig. 7 the change in reciprocal space in the course of this transition is represented schematically.

Cooling down to LNT indicates that  $(h k u)$  type reflections tend to vanish as it is the case in  $\text{RbFeF}_4$ , as can be seen in Fig. 8.

## 2.2. Decomposition under Electron Irradiation

The investigated compounds prove to be sensitive to decomposition under electron irradiation, probably through temperature-

driven evaporation of fluorine. This evaporation forces the  $BX_6$  octahedra to become locally edge-sharing giving rise to dislocationlike configurations thus deforming the lattice which upon convolution with the undistorted lattice could give rise to the moiré fringes as shown in Fig. 9a.

The high resolution micrograph of  $\text{RbFeF}_4$  (Fig. 9b) along [001] shows evidence for these "dislocations" as indicated by arrows. The interpretation is based on the assumption that the columns of  $A$  cations are imaged as white dots; this was substantiated by image calculations for the  $\text{RbFeF}_4$  aristotype structure model.

## 5. Discussion

In the case of  $\text{KFeF}_4$  the present experi-

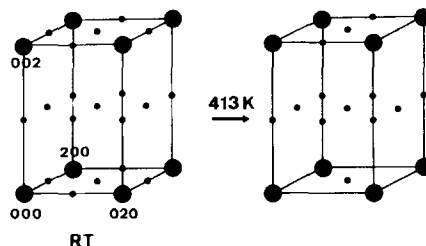


FIG. 7. Schematic representation of the phase transition at 413 K in  $\text{RbVF}_4$ .

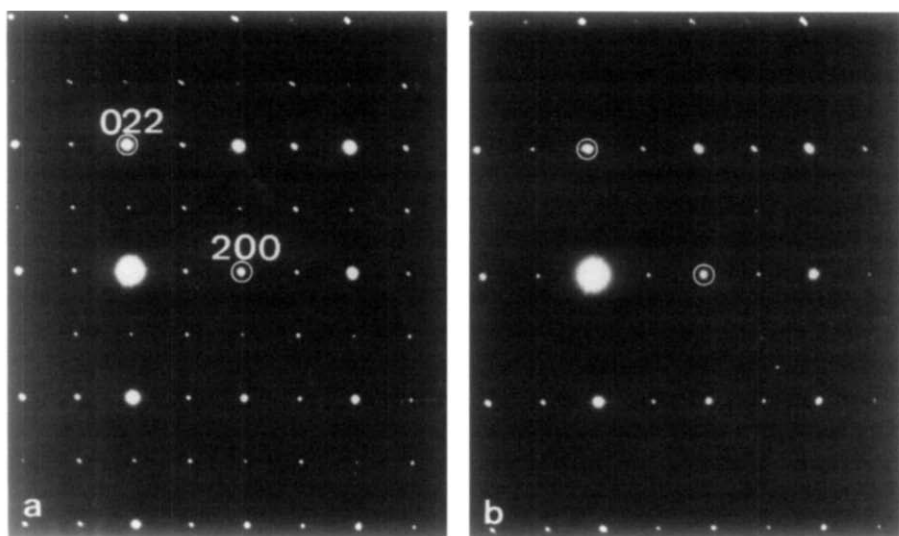
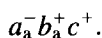


FIG. 8. The reflections of type  $(h\ k\ u)$  show tendency to vanish when cooling down to LNT in  $\text{RbVF}_4$  as can be seen in this  $[01\bar{1}]$  zone diffraction pattern.

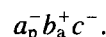
ments confirm the results of Hidaka *et al.* (5) and support therefore their interpretation. As for the transition at 413 K in  $\text{RbVF}_4$ , if it is assumed that the structure of the room temperature phase as determined by means of X-ray techniques is correct; the extended general structure symbol is



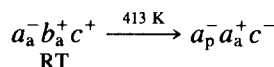
The subscripts of the extended general symbol can be determined when the diffraction typology as determined by Hidaka is compared with the complete list of all possible  $ABX_4$  hettotypes (10). This list includes the structure symbol, the space group to which the symmetry elements of the structure belong, and the diffraction typology in the approximation of rigid  $BX_6$  octahedra.

The transition toward a diffraction typology  $AYZRSM$  above 413 K can in this approach only be interpreted in terms of a vanishing or negligibly small displacement of the Rb cations.

The only structure which satisfies this demand has the tilting condition



Hence the following transformation scheme can be proposed tentatively:



The new transition between LNT and RT in  $\text{RbFeF}_4$  can be interpreted in a similar way. Several tilting schemes match the observed diffraction typology

LNT	RT
$a_p^+ a_p^+ c^0$ ( $P\ m\ m\ n$ )	$a_p^+ b_a^+ c^+$ ( $P\ m\ m\ n$ )
$a_p^+ b_p^- c^0$ ( $P\ m\ a\ b$ )	$a_p^+ b_p^- c^-$ ( $P\ m\ m\ n$ )
$a_p^+ b^0 c^+$ ( $P\ m\ m\ n$ )	$a_a^+ b_a^+ c^-$ ( $P\ m\ m\ n$ )
$a_p^+ b_p^+ c^+$ ( $P\ m\ m\ n$ )	$a_a^+ b_a^+ c^-$ ( $P\ m\ m\ n$ )
$a_p^+ b_p^- c^+$ ( $P\ 2_1/m$ )	

For the RT phase it is taken for granted that the tilting scheme proposed by Hidaka is consistent with the intensity of the reflections belonging to the  $[001]$  Laue zones of even order. It is therefore logical to retain from the above list the tilting scheme which best fits the X-ray structure refinement, which leads to

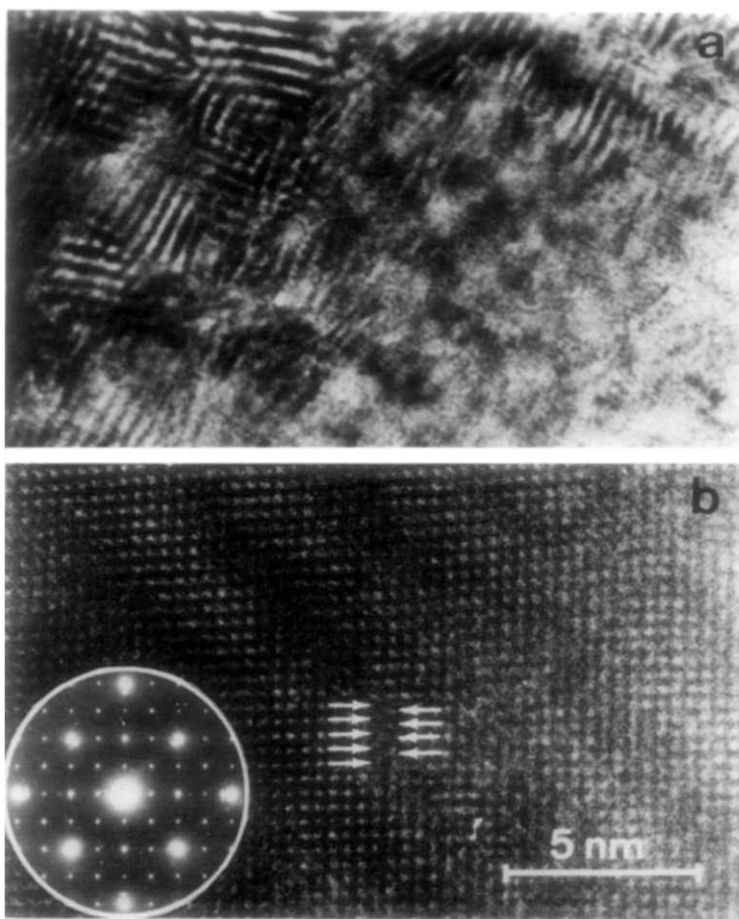
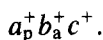
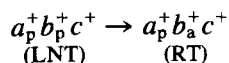


FIG. 9. (a) Moiré fringes in  $\text{RbFeF}_4$  images using the reflections of the [001] zone enclosed by the circle in (b). (b) HREM micrograph revealing the dislocationlike distortions of the octahedral network indicated by arrows.



As for the LNT phase it is not likely that when lowering the temperature a threefold tilt system reduces to a twofold one, because this would imply that an already frozen lattice mode would be excited again. It is also reasonable to suppose that the LNT phase will adopt the structure which needs the least adaptations when it has to be formed from the RT phase. This leads to the following result:



## 5. Conclusions

The present experiments generally confirm the results of the X-ray studies (5, 7, 8). In  $\text{RbVF}_4$  the doubling of the  $c$  axis remains present above the transition temperature whereas for  $\text{RbFeF}_4$  the  $c$  parameter is doubled in the RT phase and a new transition when cooling to LNT is found.

The complete list of hettotypes (10) proves to be a helpful tool in the interpretation of the structures of the different phases.

However, the reader should always keep



in mind that the present interpretation of the superstructures is based on a model taking into account only tilting of rigid octahedra and the concomitant steric displacement of the A cations because these are the most important symmetry-reducing operations.

This does not mean that the deformation of the octahedra can be neglected; in fact, the loss of inversion centers through this type of deformation has been observed (7, 8).

### Acknowledgments

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