JOURNAL OF SOLID STATE CHEMISTRY **95**, 403–411 (1991)

Structural Relations between Monoclinic and Orthorhombic Fluorite-Related Superstructures $M_{0.5-x}Ln_{0.5+x}F_{2+2x}$ Single and Twinned Phases

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Received July 15, 1991

The coefficients of a general similarity matrix which allows one to relate the fluorite structure to orthorhombic, monoclinic, and triclinic superstructures are determined for the phases $K_{0.333}Ln_{0.667}F_{2.34}$ (Ln = Y, Er, Ho, Dy, and Tb), $K_{0.333}Gd_{0.667}F_{2.34}$, $K_{0.265}Gd_{0.735}F_{2.47}$, $K_{0.25}Ln_{0.75}F_{2.50}$ (= KY_3F_{10}), and $M_{0.31}Ln_{0.69}F_{2.38}$ (M = K; Ln = Gd, Eu, Sm, Nd, Pr and M = Rb; Ln = La, Pr, Nd). The first four phases are either orthorhombic or monoclinic. They are characterized by the presence of chains of clusters Ln_6F_{36} (or Ln_6F_{37}) parallel to the direction $\mathbf{b}_F + \mathbf{c}_F$, which alternate with chains of cubes LnF_8, according to a sequence accounting for the ratio Ln/M in the phase. The juxtaposition of these chains forms layers perpendicular to the direction $\mathbf{a}_F$. Likewise, these cubes and clusters form chains parallel to the direction $[-\mathbf{b}_F + \mathbf{c}_F]$, but running alternatively at the levels 0, $1/2(\mathbf{b}_F + \mathbf{c}_F)$, 0, . . . ; they are connected by the polyhedra surrounding the alcaline cations, some of them forming chains parallel to the direction $[\mathbf{b}_F + \mathbf{c}_F]$. The fifth phase $M_{0.31}Ln_{0.69}F_{2.38}$ is triclinic. The crystals are twinned and the model of the structure which is proposed contains only bits of chains, [cluster–cube–cluster], parallel to the direction $[-\mathbf{b}_F + \mathbf{c}_F]$ and running alternatively at the levels 0, $1/4(\mathbf{b}_F + \mathbf{c}_F)$, $1/2(\mathbf{b}_F + \mathbf{c}_F)$, $3/4(\mathbf{b}_F + \mathbf{c}_F)$, 0, . . . , with substitution of the chains M–M–M · · · by chains M–Ln–M . . . . A precise determination of the structure of the fifth phase is in progress. © 1991 Academic Press, Inc.

Introduction

The study of MF–LnF_3 systems with M = K and Rb and Ln = Yttrium and lanthanides, has shown the existence of many phases, $M_{0.5-x}Ln_{0.5+x}F_{2+2x}$, which are fluorite-related superstructures; all the monoclinic or orthorhombic superlattices have the same axis $\mathbf{b}' = \mathbf{b}_F + \mathbf{c}_F$, with $\mathbf{a}_F$, $\mathbf{b}_F$, and $\mathbf{c}_F$ being the vectors of the cubic fluorite unit cell $Fm3m$.

This is the case of the orthorhombic phases $K_{0.333}Gd_{0.667}F_{2.34}$ and $K_{0.265}Gd_{0.735}F_{2.47}$, monoclinic phases $K_{0.333}Ln_{0.667}F_{2.34}$ with Ln = Y, Er, Ho, Dy, and Tb, and $M_{0.31}Ln_{0.69}F_{2.38}$ (M = K with Ln = Gd, Eu, Sm, Nd, Pr, and M = Rb with Ln = La, Pr, Nd) and triclinic twinned phases.

The object of this short note is to show the similarity of these numerous structures.

Cell Relations with the Fluorite

At first, we define an orthorhombic basis cell (parameters a_O, b_O, c_O), containing four formula units CaF_2;

0022-4596/91 $3.00

$$(\mathbf{a}, \mathbf{b}, \mathbf{c})_O = (\mathbf{a}, \mathbf{b}, \mathbf{c})_F \mathbf{S}_{FO}$$

with

$$\mathbf{S}_{FO} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & -1/2 \\ 0 & 1 & 1/2 \end{vmatrix}$$

$$\text{and } |\mathbf{S}_{FO}| = 1$$

(for notation see Bertaut *et al.* (*1*)).

This basis cell allows to describe all the superstructures (parameters a', b', c')

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c})_O \mathbf{S}$$

with

$$\mathbf{S} = \begin{vmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{vmatrix},$$

where the transformation matrix **S** is the matrix of the isomorphous subgroups (International Tables for Crystallography (*2*)). In all the transformations the $\mathbf{b}'$ axis is conserved ($\mathbf{b}' = \mathbf{b}_O = \mathbf{b}_F + \mathbf{c}_F$). Thus, in the **S** matrix, the coefficients $S_{12} = S_{32} = 0$

—in the monoclinic case $S_{21} = S_{23} = 0$. The **S** matrix has the same form as the general similarity matrix $\mathbf{M}_b$ of the monoclinic system (*2*).

—in the orthorhombic case $S_{31} = S_{13} = 0$. The **S** matrix is the $\mathbf{O}_1$ matrix (*2*).

Figure 1 schematizes cell relations between the different types of superstructures.

These superlattices are related to the fluorite face-centered cubic lattice by the relation

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c})_F \mathbf{S}_F$$

with

$$\mathbf{S}_F = \begin{vmatrix} S_{11} & 0 & S_{13} \\ -1/2S_{31} & S_{22} & -1/2S_{33} \\ 1/2S_{31} & S_{22} & {}_{1/2}S_{33} \end{vmatrix}.$$

The multiplicity m of the superstructure is defined by the ratio of the volumes V/V_F

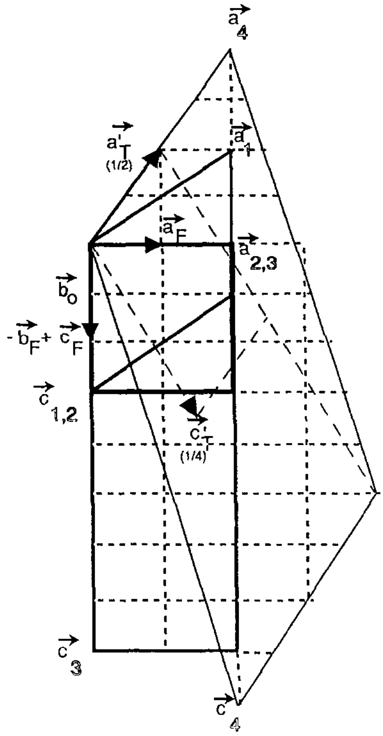

FIG. 1. Cell relations between fluorite and superstructures: (①) Phases $K_{0.333}Ln_{0.667}F_{2.34}$, (②) $K_{0.333}Gd_{0.667}F_{2.34}$, (③) $K_{0.265}Gd_{0.735}F_{2.47}$, (④) Phases $M_{0.31}Ln_{0.69}F_{2.38}$, (T) Phases $Rb_{0.31}La_{0.69}F_{2.38}$.

$$m = |\mathbf{S}_F| = |\mathbf{S}_{FO}| \cdot |\mathbf{S}|$$
$$= S_{22}[S_{11}S_{33} - S_{13}S_{31}].$$

We refer to the theory of similarity operators described by Bertaut *et al.* (*3*) concerning the symmetry operators conserved in the superstructures and defining their space groups and the suitable origins for their cells.

Table I resumes the coefficients, the multiplicities m, the space groups and the origin chosen for the structural description of the different types of phases.

Structural Characteristics

Structural studies (*4–6*) have allowed us to determine fluorite positions conserved in

TABLE I

COEFFICIENTS S_{ij} OF THE SIMILARITY MATRIX AND TRANSLATION **T**

Formula	Space group	S_{11}	S_{13}	S_{21}	S_{22}	S_{23}	S_{31}	S_{33}	m	**T**
$K_{0.333}Ln_{0.667}F_{2.333}$	*Cm*	2	0	0	1	0	−2	6	6	0, 1/4, 1/4
$K_{0.333}Gd_{0.667}F_{2.333}$	*Pmmn*	2	0	0	1	0	0	3	6	0, 0, 1/2
$K_{0.265}Gd_{0.735}F_{2.47}$	*Immm*	2	0	0	1	0	0	8	16	0, 0, 1/2
$M_{0.31}Ln_{0.69}F_{2.38}$	*Cm*	2	2	0	1	0	−4	9	26	0, 1/4, 1/4
$Rb_{0.31}La_{0.69}F_{2.38}$	*P*1	1	3/2	−1/2	1	1/4	−2	7/2	13/2	0, 1/4, 1/4
		−1	−3/2	−1/2	1	1/4	2	−7/2	13/2	
KY_3F_{10}		2	0	0	1	0	0	2	4	

the superstructures. They are related to those of fluorite by the relation

$$\mathbf{r}_{\text{superlattice}} = \mathbf{S}^{-1}[\mathbf{R}_{\text{fluorite}} - \mathbf{T}],$$

the vector **T** defining the origin of the cell.

The *cationic sublattice and a part of the anionic sublattice* F_N *of the fluorite structure are always conserved.*

But these superstructures are characterized by the existence of another anionic subcell formed by $F_{\langle 110\rangle}$ fluorine atoms observed in the anion-excess solid solutions (*7–9*). The structural determination of three types of superstructures (one monoclinic (*4*) and two orthorhombic (*6*)) has shown that these fluorine atoms always give rise to cuboctahedra $[F_{\langle 111\rangle}]_{12}$, empty (*4*), or centred by one $F_{\langle 111\rangle}$ fluorine atom (*6*), associated to six lanthanide cations. They form the central cavity of Ln_6F_{36} (or Ln_6F_{37}) clusters, the *Ln* cations being located at the centre of antiprisms formed by four $F_{\langle 110\rangle}$ fluorine atoms and four F_N "fluorite" atoms. Figure 2 schematizes one Ln_6F_{36} (or Ln_6F_{37}) cluster.

At last, structural determinations have shown that, in these types of structures, every two Ln_6F_{36} (or Ln_6F_{37}) clusters share two of their edges F_N–F_N to form chains running parallel to the direction $\mathbf{b}_F + \mathbf{c}_F$ (Fig. 3(a) and (b)).

The same succession of clusters is observed in the compound KY_3F_{10} (= $K_{0.25}Y_{0.75}F_{2.50}$) (Pierce and Hong (*10*)). This is obvious on Fig. 3(c), this phase being described with an orthorhombic cell and the coefficients indicated in Table I and recalled here:

$$(\mathbf{a}, \mathbf{b}, \mathbf{c})_O = (\mathbf{a}, \mathbf{b}, \mathbf{c})_F \left|\begin{matrix} 2 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & 1 & 1 \end{matrix}\right|.$$

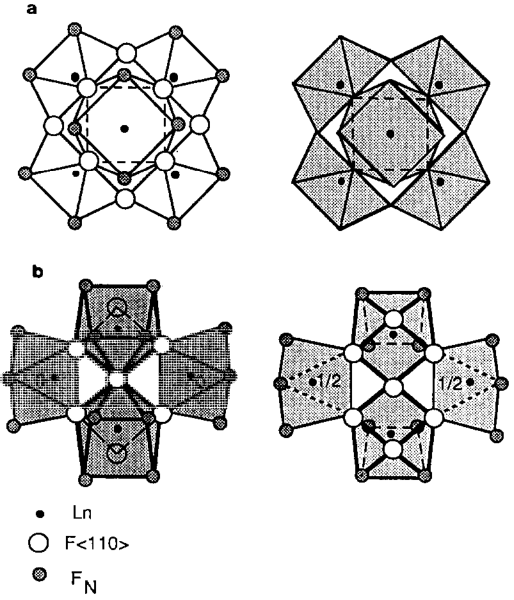

FIG. 2. Schematic projection of a cluster Ln_6F_{36} (or Ln_6F_{37}) of six square antiprisms (surrounding *Ln* atoms) sharing their $F_{\langle 110\rangle}$ corners to enclose a cuboctahedron: (a) along a pseudo four fold axis, (b) along a pseudo two fold axis.

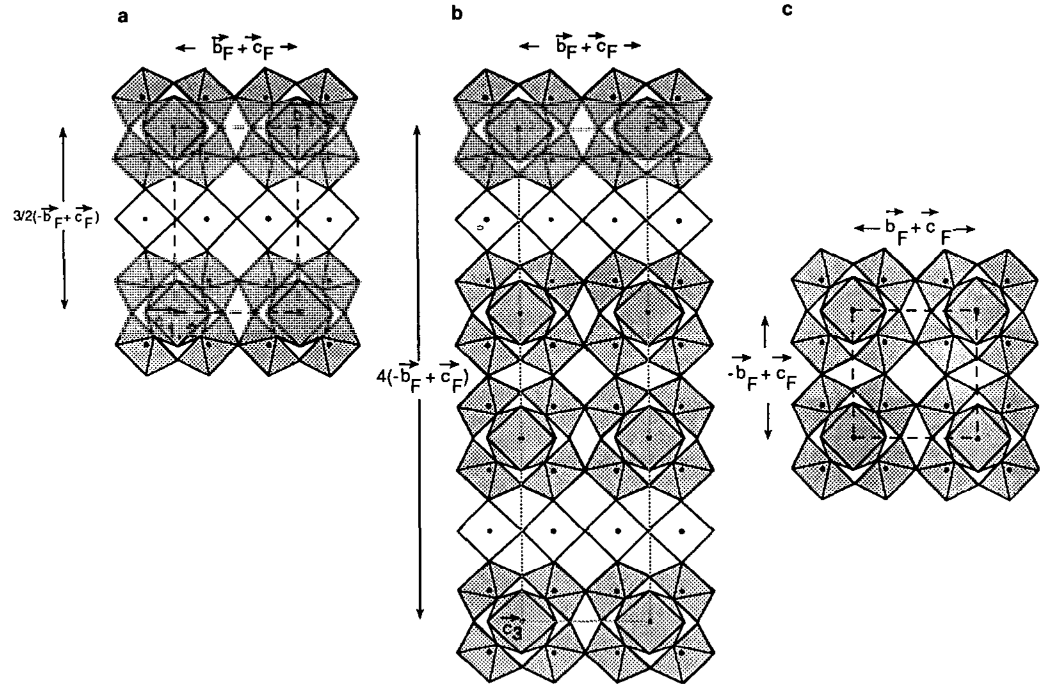

FIG. 3. Projection along the $\mathbf{a}_F$ direction of: (a) Phases $K_{0.333}Ln_{0.667}F_{2.34}$ (Ln = αY, αEr, Ho, Dy, Tb, Gd), (b) $K_{0.265}Gd_{0.735}F_{2.47}$, (c) KY_3F_{10} (= $K_{0.25}Y_{0.75}F_{2.50}$).

In the structure of $K_{0.25}Y_{0.75}F_{2.50}$, these clusters are juxtaposed in the three directions (Fig. 3(c)). But, for a ratio F/(K,Ln) below 2.5, they alternate with chains of edge-shared LnF_8 cubes, according to a sequence accounting for the ratio Ln/M in the phase:

|cluster–cube| cluster · · · with Ln/M = 2 (phases 1 and 2 (Fig. 3(a)),

|cluster–cube–cluster–cluster—cube| cluster · · · with Ln/M = 2.77 (phase 3 (Fig. 3(b))),

cluster–cluster · · · with Ln/M = 3 ($K_{0.25}Y_{0.75}F_{2.50}$ (Fig. 3(c)).

The juxtaposition of these chains forms layers perpendicular to the direction $\mathbf{a}_F$ and connected by polyhedra surrounding the alcaline cations, with the possibility for the latter ones to be occupied by a lanthanide excess, as observed in the phase 3 (*6*).

A projection of the three types of structures along the same direction $\mathbf{b}' = \mathbf{b}_F + \mathbf{c}_F$ shows that clusters and cubes form also chains perpendicular to the direction $\mathbf{a}_F$, but, in these chains the center of the cuboctahedron is alternatively at the mean levels z = 0, 1/2, 0, 1/2 · · · (Fig. 4(a), (b), (c), (d)).

The propagation of these chains create cavities in which only alcaline ions are located.

Twinned Phases

Then, concerning the phases $M_{0.31}Ln_{0.69}F_{2.38}$, we first proposed the structural model shown in the Fig. 5(a) and (b) which schematizes projections along $\mathbf{a}_F$ and $\mathbf{b}_F + \mathbf{c}_F$. This structure is completely described in the space group Cm, with its lattice origin at $\mathbf{T}$ = (0 1/4 1/4) and agreeing with the provisions of the theory of similarity operators (*3*).

Here cube and cluster chains parallel to

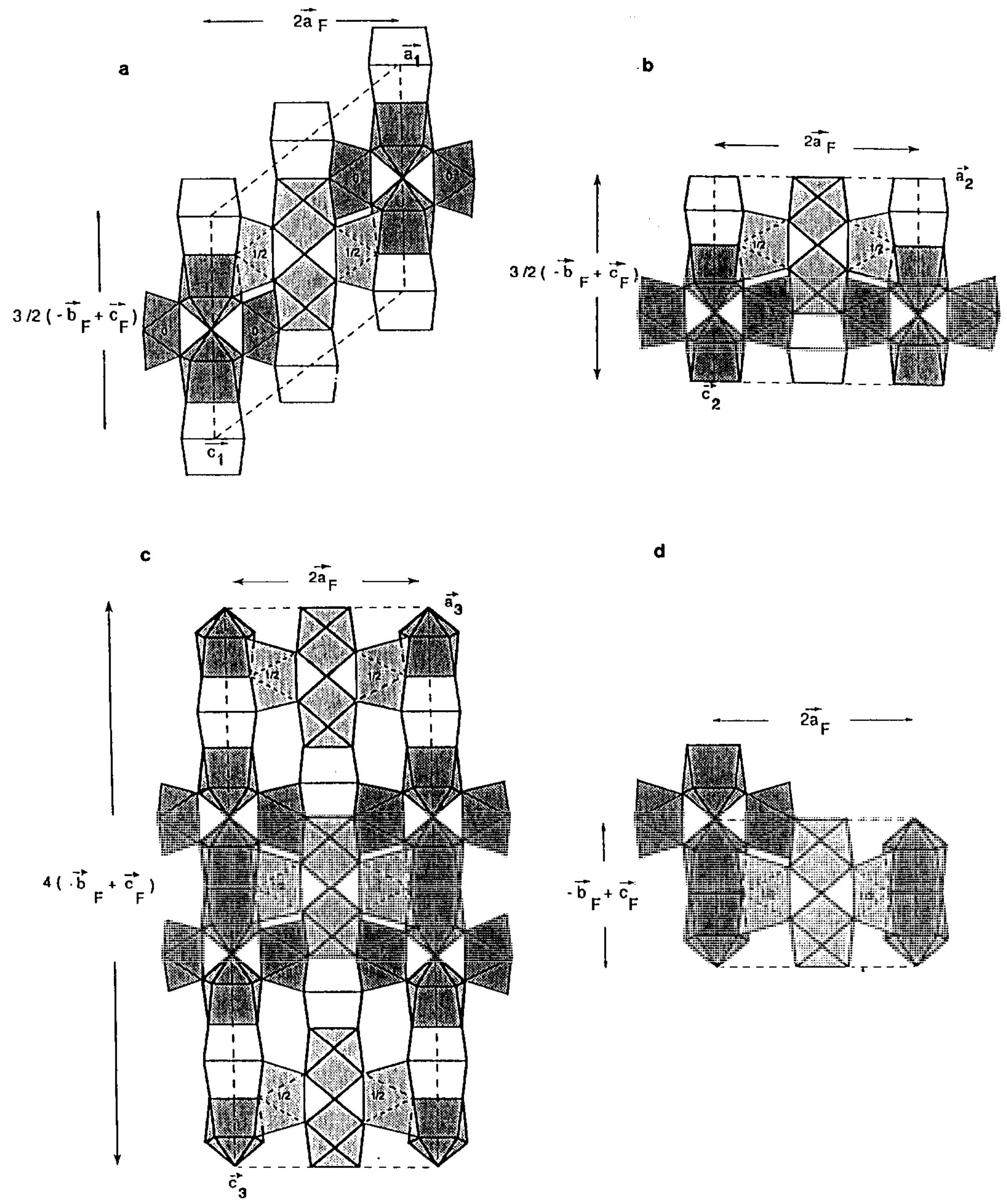

FIG. 4. Projection along the [$\mathbf{b}_F + \mathbf{c}_F$] direction of: (a) Phases $K_{0.333}Ln_{0.667}F_{2.34}$ (Ln = αY, αEr, Ho, Dy, Tb, Gd), (b) $K_{0.333}Gd_{0.667}F_{2.34}$, (c) $K_{0.265}Gd_{0.735}F_{2.47}$, (d) $K_{0.25}Ln_{0.75}F_{2.50}$ (= KLn_3F_{10}) (Ln = Y, Er, Ho, . . .).

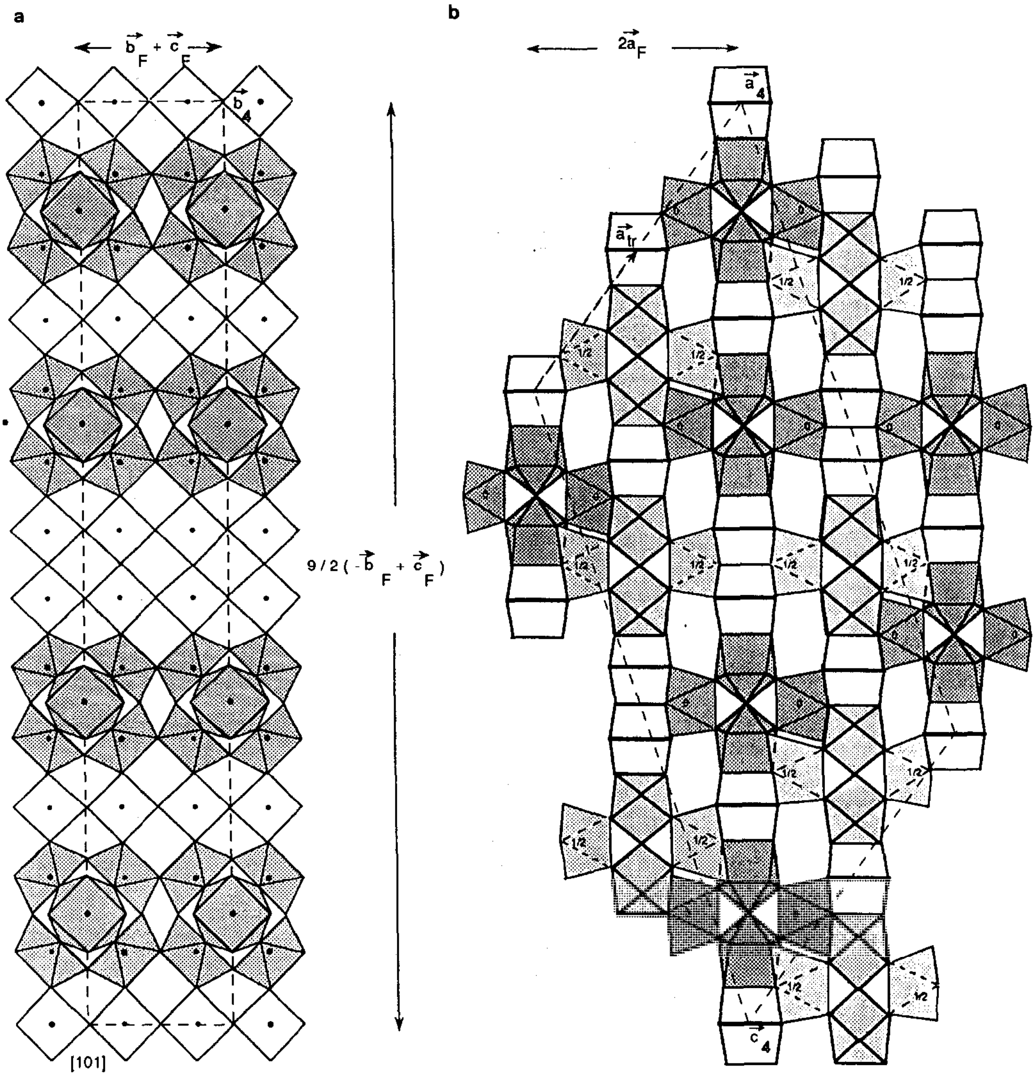

FIG. 5. First model proposed for the phases $M_{0.31}Ln_{0.69}F_{2.38}$: (a) Projection along the $\mathbf{a}_F$ direction, (b) Projection along the $\mathbf{b}_F + \mathbf{c}_F$ direction.

the direction $\mathbf{b}_F + \mathbf{c}_F$ might alternate according to the sequence: |cube–cluster–cube–cluster–cube–cube–cluster–cube–cluster–|cube–cluster · · · (Fig. 5(a)), with always, along $\mathbf{a}_F$, an alternative juxtaposition of chains cluster–cube · · · at the mean levels 0, 1/2, 0, 1/2. . . .

Such a model has been refined to the R factor = 0.10, with a partial occupation of the alcaline sites by a lanthanide excess (like in phase 3) and a fluorine atom at the center of the eight clusters of the lattice. A statistic disorder alcaline–rare earth in all the sites might lead to a smaller R factor.

But, with the rubidium and lanthanum, the study of a single crystal of this phase,

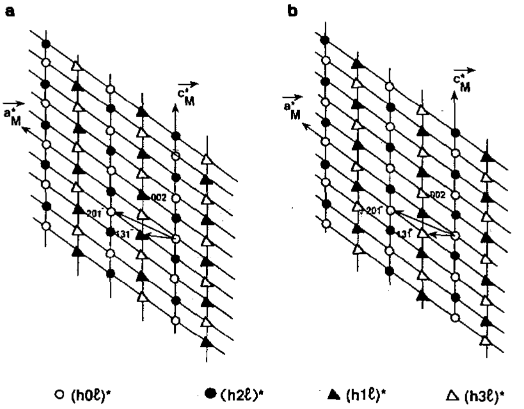

FIG. 6. Reciprocal network of $Rb_{0.31}La_{0.69}F_{2.38}$. (a) Individual I, (b) Individual II, related to the first one by a rotation about $\mathbf{b}^*_m$.

has shown that the monoclinic lattice $a' = 20.82$ Å, $b' = 8.44$ Å, $c' = 39.98$ Å, $\beta = 125.97°$, was that of a twinned crystal. The systematic extinctions observed on the electronic diffraction patterns and schematized on Fig. 6(a),

$$00l : l = 2n + 1; \quad 20l : l = 2n; \quad 40l : l = 2n + 1; \cdots$$

$$02l : l = 2n; \quad 04l : l = 2n + 1; \quad 06l : l = 2n; \cdots$$

$$11l : l = 2n \quad 13l : l = 2n + 1; \quad 15l : l = 2n; \cdots$$

$$-11l : l = 2n + 1; \quad -13l : l = 2n; \quad -15l : l = 2n + 1; \ldots,$$

showed the presence of two individuals related by a rotation about the monoclinic axis $\mathbf{b}'$ (Fig. 6(a) and (b)).

The relations between the reciprocal lattices of each individual and the twinned crystal are,

—individual I:

$$\left|\begin{matrix} a'^* \\ b'^* \\ c'^* \end{matrix}\right| = \left|\begin{matrix} 2 & 0 & -1 \\ 1 & 1 & -1 \\ 0 & 0 & 2 \end{matrix}\right| \left|\begin{matrix} a'^* \\ b'^* \\ c'^* \end{matrix}\right|_M$$

—individual II:

$$\left|\begin{matrix} a'^* \\ b'^* \\ c'^* \end{matrix}\right| = \left|\begin{matrix} -2 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & 0 & -2 \end{matrix}\right| \left|\begin{matrix} a'^* \\ b'^* \\ c'^* \end{matrix}\right|_M,$$

and in the direct space,

$$[\mathbf{a}', \mathbf{b}', \mathbf{c}']_{\mathrm{I}} = [\mathbf{a}, \mathbf{b}, \mathbf{c}]_{\mathbf{M}} \mathbf{S}^{\mathrm{I}}_{\mathbf{MT}}$$

with

$$\mathbf{S}^{\mathrm{I}}_{\mathbf{MT}} = \left|\begin{matrix} 1/2 & 0 & 1/4 \\ -1/2 & 1 & 1/4 \\ 0 & 0 & 1/2 \end{matrix}\right|$$

and

$$[\mathbf{a}', \mathbf{b}', \mathbf{c}']_{\mathrm{II}} = [\mathbf{a}, \mathbf{b}, \mathbf{c}]_{\mathbf{M}} \mathbf{S}^{\mathrm{II}}_{\mathbf{MT}}$$

with

$$\mathbf{S}^{\mathrm{II}}_{\mathbf{MT}} = \left|\begin{matrix} 1/2 & 0 & -1/4 \\ -1/2 & 1 & 1/4 \\ 0 & 0 & -1/2 \end{matrix}\right|.$$

The coefficients of the **S** matrix are given in Table I.

The dimensions of the triclinic lattice of each individual are:

$$a = 11.22 \text{ Å}, b = 8.45 \text{ Å}, c = 17.549 \text{ Å},$$

$$\alpha = 83.08°, \beta = 112.93°, \gamma = 112.11°.$$

In view of the previous structural hypothesis, we now propose the model shown on Fig. 7(b). This figure schematizes the projection of this triclinic structure along the direction $\mathbf{b}_{\mathrm{M}}$, and indicates the coordinates of the two triclinic axes $\mathbf{a}'_{\mathrm{T}}$ (level 1/2) and $\mathbf{c}'_{\mathrm{T}}$ (level 1/4). Their relation with the other superstructures is shown in Fig. 1.

This structure would retain only parts of chains |cluster–cube–cluster| · · · parallel to the direction $[-\mathbf{b}_{\mathrm{F}} + \mathbf{c}_{\mathrm{F}}]$ and running in the direction $\mathbf{a}_{\mathrm{F}}$ at the alternative level $b' = 0, 1/4, 1/2, 3/4, 1. \ldots$ (Fig. 7(a) and (b)).

Such a model may perfectly agree with the formula $Rb_8La_{18}F_{62}$, if, along the direction $\mathbf{b}_{\mathrm{M}}$ and between chains |clusters–

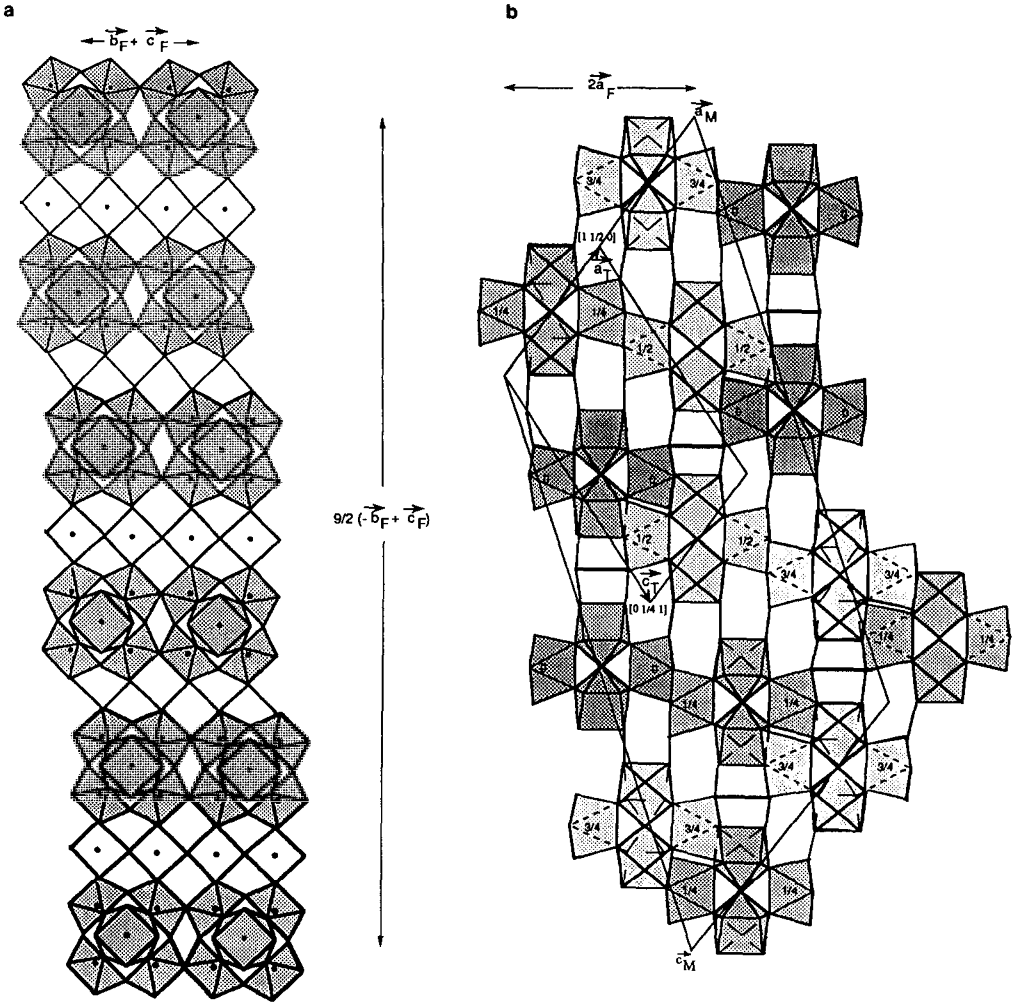

FIG. 7. Phases $M_{0.31}Ln_{0.69}F_{2.38}$: (a) Projection along the $\mathbf{a}_F$ direction, (b) Projection along the $[\mathbf{b}_F + \mathbf{c}_F]$ direction.

cubes–clusters| . . . , the Rb–Rb–Rb · · · superposition observed in the single phases are replaced by the sequence Rb–La–Rb. . . .

The observed intensities are in favor of the presence of two individuals in equal proportion. After selection of intensities of only one individual, this cationic model has been refined to a R factor = 0.09, with suitable thermal factors.

The study of an untwinned crystal should confirm these results.

Conclusion

The study of the fluorite-related fluorine compounds shows that the cationic frame is preserved, the anions being displaced significantly from ideal fluorine. The present paper which describes monoclinic, orthorhombic, and triclinic superstructures points out that the similarity operators are very useful to get a systematic classification of may connected structures and evidence their particularities.

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