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The Use of Similarity Operators for Lattice–Superlattice Relations

I. Applications to Monoclinic and Orthorhombic Fluorite-Related Structures*

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Similarity operators are shown to relate the lattice vectors and origins of the structure and the superstructure, the symmetry operators of the space group G of the structure to those of the subgroup H of G of the superstructure, and finally those atomic positions which are conserved in the superstructure. In the monoclinic and orthorhombic fluorite-related structures of compositon $K_{0.5-x}Ln_{0.5+x}F_{2+2x}$ (Ln = lanthanide and Y) considered here we find that the cation sublattice is conserved. The origin of the superstructure does not necessarily coincide with the origin of the structure, but is a point of high site symmetry. © 1988 Academic Press, Inc.

Introduction

In a preceding paper (*1*), fluoride compounds of the family $K_{0.5-x}Ln_{0.5+x}F_{2+2x}$ (Ln = lanthanide and Y) were discussed and relations between the cell vectors of the fluorite cell and various supercells were obtained from high-resolution electron diffraction diagrams.

Using similarity operators we shall show that these vectorial relations between cells and supercells impose strong constraints on possible centerings and symmetry elements and thus on the space groups possible for fluorite-related structures.

Similarity Operators

Generalities

Similarity operators have been designed first for deriving equivalent or isomorphic subgroups of a space group G, e.g., groups which conserve the Hermann–Mauguin symbol of G (*2, 3*).

Their use has been extended by one of us to the study of displacive transitions, e.g., transitions from a space group G to a subgroup H (*4*) which is no longer isomorphic.

In the present paper we apply similarity operators for relating a so-called superstructure to a given structure type for which we have chosen the fluorite type.

In part I we consider monoclinic and orthorhombic superlattices and in part II tetragonal and rhombohedral superlattices.

Definitions and Notations

We shall state the main properties without the proofs, which are given in the references (*2–4*). We use a structure described in a reference frame (O, **a**, **b**, **c**) and belonging to a space group G, the fluorite structure. O is the origin, **a**, **b**, **c** the vectors of the unit cell. Here $G = Fm3m$.

On the other hand, we have a so-called

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"superstructure," described in a reference frame (O′, **a**′, **b**′, **c**′) and belonging to a space group H which is a subgroup of G. (The name of "superstructure" and of "superlattice" is rather unfortunate, substructure and sublattices would be more convenient for designing a structure which belongs to H and which has a translation group γ, subgroup of the translation group Γ of G.) The origins O and O′ may coincide, but in general do not.

Between the cell vectors one has a relation

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c})\, S, \qquad (1)$$

where S is a 3×3 matrix; (**a**′, **b**′, **c**′) and (**a**, **b**, **c**) are *row* matrices 3×1. The relation (1) is not particularly new. It is found in the literature (see, for instance, (*1*)) but written for the cell vectors in *column* matrices. We shall however stick to the convention (1) not only because it has been adopted in the new "International Tables" (*5*) but mainly because column vectors will be used in the following for another purpose, that of finding centerings and coordinate triplets. We shall denote the origin separation OO′ by a coordinate triplet T.

$$T = \begin{bmatrix} X_{O'} \\ Y_{O'} \\ Z_{O'} \end{bmatrix}. \qquad (2)$$

Here $X_{O'}$, $Y_{O'}$, $Z_{O'}$, are the coordinates of the origin O′ in the reference frame of G. By definition, the operator $\mathcal{S}$ shall be called the *similarity operator*:

$$\mathcal{S} = (S|T). \qquad (3)$$

It is important to state here that the similarity operator $\mathcal{S}$ has the same structure as the symmetry operator. Let a be a symmetry operator of G. Here α is a 3×3 matrix (the "rotational" part) and τ_α the translational part, written as a column matrix:

$$a = (\alpha|\tau_\alpha). \qquad (4)$$

If R is a point specified by the coordinate triplet (Eq. (5)) in the reference frame of G, then by definition, the action of a on R results in a new point R' given by Eq. (6):

$$R = \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \qquad (5)$$

$$r_0 = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \qquad (5')$$

$$R' = aR = \alpha R + \tau_\alpha. \qquad (6)$$

We are now prepared for two particularly important relations. The first one relates the point R (Eq. (5)), expressed in the reference frame (O, **a**, **b**, **c**) of G, to the same point r_0 (Eq. (5′)), expressed in the reference frame (O′, **a**′, **b**′, **c**′) of H:

$$R = \mathcal{S} r_0 = S r_0 + T. \qquad (7)$$

Inversely one has

$$r_0 = S^{-1}(R - T). \qquad (7')$$

The second important equation relates a symmetry operator a expressed in the reference frame (O, **a**, **b**, **c**) of G to the *same* symmetry operator b expressed in the reference frame (O′, **a**′, **b**′, **c**′) of H under the condition that it is conserved in the subgroup H (see below):

$$a\mathcal{S} = \mathcal{S}b. \qquad (8)$$

Here one has (cf. Eq. (4))

$$b = (\beta|\tau_\beta). \qquad (4')$$

Splitting the rotational and translational parts of Eq. (8), one obtains the relation (Eq. (8′)) between the matrices α, β, and S and the relation (Eq. (8″)) between the translation τ_α, τ_β, and T:

$$\alpha S = S\beta \quad \text{or} \quad \beta = S^{-1}\alpha S \qquad (8')$$

$$\tau_\alpha = S\tau_B + (\mathbf{1} - \alpha)T. \qquad (8'')$$

Here **1** is the matrix unity. For pure translations one has $\alpha = \mathbf{1}$ and Eq. (8″) reduces to

$$\tau_\alpha = S\tau_\beta. \tag{9}$$

Finally we calculate the relation between reciprocal lattice vectors:

$$\begin{bmatrix} \mathbf{a}'^* \\ \mathbf{b}'^* \\ \mathbf{c}'^* \end{bmatrix} = S^{-1} \begin{bmatrix} \mathbf{a}^* \\ \mathbf{b}^* \\ \mathbf{c}^* \end{bmatrix} \quad \text{or} \quad S \begin{bmatrix} \mathbf{a}'^* \\ \mathbf{b}'^* \\ \mathbf{c}'^* \end{bmatrix} = \begin{bmatrix} \mathbf{a}^* \\ \mathbf{b}^* \\ \mathbf{c}^* \end{bmatrix}. \tag{10}$$

The procedure is then as follows. From relation (10) in reciprocal space, from the diffraction pattern, one gets the matrices S^{-1} and S and thus the relation (Eq. (1)) between the cell vectors in direct space.

Knowing the centering translations τ_α in G, relation (9) will tell us what centerings τ_β, if any, are possible in the "superlattice," e.g., in subgroup H.

From the knowledge of the matrices α of the crystal class of G, we compute the matrices β by means of relation (8′), a matrix β is "allowed" in subgroup H if its coefficients β_{ij} are $+1$, -1, or 0. The study of relation (8″) specifies possible choices of the origin O′ and of the fractional translations τ_β (for more details see Refs. (*2–4*)).

Finally we synthesize the resulting information in the indication of possible space groups and atomic positions.

The α-Matrices

The fluorite structure belongs to the crystal class $m3m$. Instead of printing the 48 matrices of the point group, we only recall their general structure.

There are diagonal matrices:

$$\alpha_1 = \begin{bmatrix} \varepsilon_1 & \cdot & \cdot \\ \cdot & \varepsilon_2 & \cdot \\ \cdot & \cdot & \varepsilon_3 \end{bmatrix}. \tag{11}$$

Trivial cases are the identity operator **1** with $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = +1$ and the inversion operator $\bar{\mathbf{1}}$ with $\varepsilon_j = -1$ ($j = 1, 2, 3$). The nontrivial matrices α_1 correspond either to twofold rotations around the coordinate axes or to mirrors perpendicular to them. The next matrices to be considered have only one diagonal element:

$$\alpha_{2,1} = \begin{bmatrix} \varepsilon_1 & \cdot & \cdot \\ \cdot & \cdot & \varepsilon_2 \\ \cdot & \varepsilon_3 & \cdot \end{bmatrix};$$

$$\alpha_{2,2} = \begin{bmatrix} \cdot & \cdot & \varepsilon_1 \\ \cdot & \varepsilon_2 & \cdot \\ \varepsilon_3 & \cdot & \cdot \end{bmatrix}; \tag{12}$$

$$\alpha_{2,3} = \begin{bmatrix} \cdot & \varepsilon_1 & \cdot \\ \varepsilon_2 & \cdot & \cdot \\ \cdot & \cdot & \varepsilon_3 \end{bmatrix}.$$

According to the signs of the ε_j, they represent diagonal mirrors or diagonal twofold rotations or fourfold rotations. Finally we have matrices which have no diagonal element at all and represent threefold rotations:

$$\alpha_{3,1} = \begin{bmatrix} \cdot & \cdot & \varepsilon_1 \\ \varepsilon_2 & \cdot & \cdot \\ \cdot & \varepsilon_3 & \cdot \end{bmatrix};$$

$$\alpha_{3,2} = \begin{bmatrix} \cdot & \varepsilon_1 & \cdot \\ \cdot & \cdot & \varepsilon_2 \\ \varepsilon_3 & \cdot & \cdot \end{bmatrix}. \tag{13}$$

Monoclinic Phases

KHo_2F_7. We illustrate the procedure in the example of KHo_2F_7 (*1*). All reflections could be indexed in a reciprocal lattice $\mathbf{a}'^*$, $\mathbf{b}'^*$, $\mathbf{c}'^*$ related to the reciprocal lattice vectors $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ of the fluorite cell by the following relations (*1*):

$$\mathbf{a}'^* = \tfrac{1}{2}\mathbf{a}^*; \quad \mathbf{b}'^* = \tfrac{1}{2}(\mathbf{b}^* + \mathbf{c}^*);$$
$$\mathbf{c}'^* = \tfrac{1}{3}(\mathbf{a}^* - \mathbf{b}^* + \mathbf{c}^*). \tag{14}$$

From Eq. (10) one has at once the matrix S^{-1}. The matrix S is obtained either by solving the system above with respect to $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ or by inverting S^{-1}:

$$S^{-1} = \begin{bmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{3} & -\frac{1}{3} & \frac{1}{3} \end{bmatrix}, \qquad S = \begin{bmatrix} 2 & 0 & 0 \\ 1 & 1 & -\frac{3}{2} \\ -1 & 1 & \frac{3}{2} \end{bmatrix}. \tag{15}$$

The relations between cell vectors in direct space (cf. Eq. (1)) and angles become

$$\mathbf{a}' = 2\mathbf{a} + \mathbf{b} - \mathbf{c}; \quad \mathbf{b}' = \mathbf{b} + \mathbf{c};$$
$$\mathbf{c}' = \tfrac{3}{2}(-\mathbf{b} + \mathbf{c}) \tag{14'}$$
$$\alpha' = \gamma' = 90°; \quad \beta' = 125°.$$

We now insert into relation (9) centering translations $0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ for τ_β and examine whether they give rise to possible lattice translations τ_α. One finds

$$S\begin{bmatrix} 0 \\ \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} = \begin{bmatrix} 0 \\ -\frac{1}{4} \\ \frac{1}{4} \end{bmatrix}; \quad S\begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \end{bmatrix} = \begin{bmatrix} 1 \\ -\frac{1}{4} \\ +\frac{1}{4} \end{bmatrix};$$
$$S\begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix}; \quad S\begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} = \begin{bmatrix} 1 \\ \frac{1}{4} \\ \frac{3}{4} \end{bmatrix}, \tag{16}$$

so that the only centering allowed in H is the C-centering $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0)$.

The β-Matrices

The evaluation of the matrices $S^{-1}\alpha S$ according to Eq. (8') is rather automatic. We only give one example. One has, for instance,

$$\beta_{2,1} = S^{-1}\alpha_{2,1}S = \begin{bmatrix} \varepsilon_1 & 0 & 0 \\ \frac{1}{2}(-\varepsilon_2 + \varepsilon_3) & \frac{1}{2}(\varepsilon_2 + \varepsilon_3) & \frac{3}{4}(\varepsilon_2 - \varepsilon_3) \\ \frac{1}{3}(2\varepsilon_1 + \varepsilon_2 + \varepsilon_3) & \frac{1}{3}(-\varepsilon_2 + \varepsilon_3) & -\frac{1}{2}(\varepsilon_2 + \varepsilon_3) \end{bmatrix}. \tag{17}$$

The fact that the matrix coefficients can only be 0, +1, and −1 implies that $\varepsilon_2 = \varepsilon_3$ and $\varepsilon_2 = -\varepsilon_1$ so that

$$\beta_{2,1} = \begin{bmatrix} \varepsilon_1 & \cdot & \cdot \\ \cdot & -\varepsilon_1 & \cdot \\ \cdot & \cdot & \varepsilon_1 \end{bmatrix} \text{ in } H \text{ is the image of } \alpha_{2,1} = \begin{bmatrix} \varepsilon_1 & \cdot & \cdot \\ \cdot & \cdot & -\varepsilon_1 \\ \cdot & -\varepsilon_1 & \cdot \end{bmatrix} \text{ in } G. \tag{17'}$$

Thus one is left with a mirror operation for $\varepsilon_1 = +1$:

$$\beta = \begin{bmatrix} 1 & \cdot & \cdot \\ \cdot & -1 & \cdot \\ \cdot & \cdot & 1 \end{bmatrix} \text{ and/or a twofold rotation } \beta = \begin{bmatrix} -1 & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & -1 \end{bmatrix} \text{ for } \varepsilon_1 = -1. \tag{17''}$$

For the sake of concision we only state the results. The evaluation of $S^{-1}\alpha_1 S$ gives rise to the trivial β matrices **1** and $\bar{\mathbf{1}}$. The evaluation of $S^{-1}\alpha S$ with the matrices $\alpha_{2,2}$, $\alpha_{2,3}$, $\alpha_{3,1}$, and $\alpha_{3,2}$ gives rise to matrices with fractional coefficients so that the corre-

sponding symmetry operations of G are not conserved in H.

Choice of the Origin

The discussion is based on Eq. (8″). One has, for $\alpha = m$, a diagonal mirror:

$$\mathbf{1} - \alpha = \begin{bmatrix} \cdot & \cdot & \cdot \\ \cdot & 1 & 1 \\ \cdot & 1 & 1 \end{bmatrix} \tag{18}$$

and

$$(\mathbf{1} - \alpha)T = \begin{bmatrix} 0 \\ T' \\ T' \end{bmatrix}. \tag{18'}$$

Here we have abbreviated

$$T' = Y_{O'} + Z_{O'}. \tag{18''}$$

Finally, the three components of τ_α (Eq. (8″)) are

$$\begin{aligned} (\tau_\alpha)_x &= 2(\tau_\beta)_x \\ (\tau_\alpha)_y &= (\tau_\beta)_x + (\tau_\beta)_y - \tfrac{3}{2}(\tau_\beta)_z + T' \\ (\tau_\alpha)_z &= -(\tau_\beta)_x + (\tau_\beta)_y + \tfrac{3}{2}(\tau_\beta)_z + T'. \end{aligned} \tag{19}$$

In principle, the matrix

$$\alpha_{2,1} = m = \begin{bmatrix} 1 & \cdot & \cdot \\ \cdot & \cdot & -1 \\ \cdot & -1 & \cdot \end{bmatrix}$$

can be associated with the translations τ_α = 0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0. In fact, the translations $\frac{1}{2}$, 0, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, 0 can be discarded for τ_α because they imply $(\tau_\beta)_x = \frac{1}{4}$ which is not admissible ($\frac{1}{4}$ only occurs in cubic groups (*d* planes)). Thus, we are left with the discussion of $(m|\tau_\alpha)$ for τ_α = 0, 0, 0 and τ_α = 0, $\frac{1}{2}$, $\frac{1}{2}$ which both are true mirror operations.

Case τ_α = 0, 0, 0 (modulo integer). The equations are satisfied for τ_β = 0, 0, 0 and as well for $\tau_\beta = \frac{1}{2}, \frac{1}{2}, 0$ with $T' = 0$. In this case, the origins O and O′ may coincide.

Case τ_α = 0, $\frac{1}{2}$, $\frac{1}{2}$. The equations are still satisfied for τ_β = 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, 0$ with $T' = \frac{1}{2}$. Thus one may choose $Y_{O'} = Z_{O'} = \frac{1}{4}$.

Finally, we are left with the choice between space groups $C2$, Cm, and $C2/m$ and two possible origins O′.

In fact, the structure itself has already been established in space group Cm (*6*) and belongs to the so-called α-KEr_2F_7 type which is also encountered for the heavy rare earths Ho, Dy, Tb. The comparison shows that *all cation positions are conserved* and that O′ is in 0, $\frac{1}{4}$, $\frac{1}{4}$.

The 8 K ions are on the mirror m in four Wyckoff positions 2a (x, 0, z) of Cm.

Of 16 Ho ions, 4 are on the mirror m in two positions 2a and 12 are accommodated in three positions 4b (x, y, z; x, $-y$, z).

Note that atoms on the mirror m have coordinates XYZ in the reference frame (O, **a**, **b**, **c**) such that $Y + Z = \frac{1}{2}$.

The correspondence between the ideal positions in H and in G is given by:

$$r_0 = \begin{bmatrix} x_0 \\ y_0 \\ z_0 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{3} & -\frac{1}{3} & \frac{1}{3} \end{bmatrix} \begin{bmatrix} X \\ Y - \frac{1}{4} \\ Z - \frac{1}{4} \end{bmatrix} = \begin{bmatrix} \frac{1}{2}X \\ \frac{1}{2}(Y + Z) - \frac{1}{4} \\ \frac{1}{3}(X - Y + Z) \end{bmatrix}. \tag{20}$$

It is noteworthy to mention that of 56 F ions in the unit cell, 32 conserve their positions (atoms (1) to (6), (8) to (10), (17) to (19) in (*6*)) and 24 are significantly displaced (atoms (7) and (11) to (16)).

KLn_2F_7. Paper (*1*) also reports a compound of the same composition KLn_2F_7, called "phase B," where *Ln* is a light rare earth Pr, Nd, Sm, Eu, Gd. The reciprocal lattice relations are

$$\begin{aligned} \mathbf{a}'^* &= \tfrac{1}{26}(5\mathbf{a}^* + 4(\mathbf{b}^* - \mathbf{c}^*)), \\ \mathbf{b}'^* &= \tfrac{1}{2}(\mathbf{b}^* + \mathbf{c}^*), \\ \mathbf{c}'^* &= \tfrac{1}{13}(2\mathbf{a}^* - (\mathbf{b}^* - \mathbf{c}^*)). \end{aligned} \tag{21}$$

The S matrix is

$$S = \begin{bmatrix} 2 & 0 & 4 \\ 2 & 1 & -\frac{5}{2} \\ -2 & 1 & \frac{5}{2} \end{bmatrix}. \quad (22)$$

The direct lattice relations are

$$\mathbf{a}' = 2(\mathbf{a} + \mathbf{b} - \mathbf{c}), \quad \mathbf{b}' = (\mathbf{b} + \mathbf{c}),$$
$$\mathbf{c}' = 4\mathbf{a} + \tfrac{5}{2}(-\mathbf{b} + \mathbf{c}), \quad (21')$$

and one finds $\alpha' = \gamma' = 90°$, $\cos \beta' = -2/(3\sqrt{38})$, say $\beta'_{calc} = 96.2°$, the observed value being $\beta'_{obs} = 97.42°$.

We leave it as an exercise to the reader to show that the only symmetry element which is conserved is a mirror and/or a twofold rotation axis as in the case discussed above and that the only space groups to be discussed are Cm, $C2$, and $C2/m$. There is no doubt that the use of similarity operators will speed up the elucidation of the structure.

Orthorhombic Phases

Finally we present the procedure for the compound $K_{0.5-x}Gd_{0.5+x}F_{2+2x}$ with $2x = 0.47$, e.g., $K_{0.265}Gd_{0.735}F_{2.47}$ called "phase A" in paper (*1*).

The reciprocal lattice relations are (*1*)

$$\mathbf{a}'^* = \tfrac{1}{2}\mathbf{a}^*, \quad \mathbf{b}'^* = \tfrac{1}{2}(\mathbf{b}^* + \mathbf{c}^*),$$
$$\mathbf{c}'^* = \tfrac{1}{8}(-\mathbf{b}^* + \mathbf{c}^*). \quad (23)$$

The matrices S^{-1} and S are found to be

$$S^{-1} = \begin{bmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & -\frac{1}{8} & \frac{1}{8} \end{bmatrix},$$

$$S = \begin{bmatrix} 2 & 0 & 0 \\ 0 & 1 & -4 \\ 0 & 1 & 4 \end{bmatrix} \quad (24)$$

so that

$$\mathbf{a}' = 2\mathbf{a}, \quad \mathbf{b}' = \mathbf{b} + \mathbf{c},$$
$$\mathbf{c}' = 4(-\mathbf{b} + \mathbf{c}). \quad (23')$$

All centerings A, B, C, F, and I are compatible with relation (9), the experiment (*1*) showing that the translation group is definitely I ($h + k + l = 2n$).

The matrices α which have images β are such that

$$\alpha_1 = \beta_1 = \begin{bmatrix} -1 & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & 1 \end{bmatrix} = m_x \quad (25)$$

$$(\alpha_{2,1})_1 = \begin{bmatrix} 1 & \cdot & \cdot \\ \cdot & \cdot & -1 \\ \cdot & -1 & \cdot \end{bmatrix} \rightarrow$$

$$\beta = \begin{bmatrix} 1 & \cdot & \cdot \\ \cdot & -1 & \cdot \\ \cdot & \cdot & 1 \end{bmatrix} = m_y \quad (26)$$

$$(\alpha_{2,1})_2 = \begin{bmatrix} 1 & \cdot & \cdot \\ \cdot & \cdot & 1 \\ \cdot & 1 & \cdot \end{bmatrix} \rightarrow$$

$$\beta = \begin{bmatrix} 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & -1 \end{bmatrix} = m_z. \quad (27)$$

The highest symmetry group which can be inferred is *Immm*.

The structure analysis given in another paper (*7*) has shown that all cation positions are near to the ideal positions given by

$$r_0 = S^{-1}(R - T).$$

Here $T = 0, 0, \frac{1}{2}$ is the coordinate triplet of the origin O′ of the superstructure in the reference frame (O, **a**, **b**, **c**) of the fluorite structure. For instance, for the cation at $R = 0, 0, 0$, one has $r_0 = 0, -\frac{1}{4}, -\frac{1}{16}$. The formula corresponding to the unit cell turns out to be $K_{17}Gd_{47}F_{158}$, e.g., $M_{64}F_{158}$, so that there are 30 excess F anions.

The Gd cations are ordered in the following positions of space group *Immm*: four positions 8e $\pm(0, y, z)$ with $y_j \sim \frac{1}{4}(j = 1, 2,$

3, 4), $z_1 \sim \frac{1}{16}$; $z_2 \sim \frac{3}{16}$, $z_3 \sim \frac{5}{16}$, $z_4 \sim \frac{7}{16}$; positions 8m $\pm(x, 0, z)$ with $x \sim \frac{1}{4}$, $z \sim \frac{3}{8}$; and positions 4e $\pm(x, 0, 0)$ with $x \sim \frac{1}{4}$. The K cations are ordered in 8m $\pm(x, 0, z)$ with $x \sim \frac{1}{4}$, $z \sim \frac{1}{8}$ and 4f $\pm(x, \frac{1}{2}, 0)$ with $x \sim \frac{1}{4}$. Finally there is one mixed site 8m $\pm(x, 0, z)$ with $x \sim \frac{1}{4}$, $z \sim \frac{1}{4}$, occupied by 3 Gd and 5 K atoms.

Remark on the Origin of the Superstructure

Our study has shown that the origin O′ of the superstructure has coordinates $0, \frac{1}{4}, \frac{1}{4}$ in the case of KHo_2F_7 and coordinates $0, 0, \frac{1}{2}$, or equivalently $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ in the case of $K_{0.265}Gd_{0.735}F_{2.47}$ with respect to the fluorite reference frame. A glance at the International Tables (*5*) shows that in space group $Fm3m$, the point $0, \frac{1}{4}, \frac{1}{4}$ under 4d has point symmetry mmm and the point $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ under 4b has (the highest) point symmetry $m3m$. In both cases we have positions which are unoccupied in the fluorite structure, but which have a high point symmetry.

In the superstructure the point O′ is not occupied in KHo_2F_7 while in the orthorhombic compound $K_{0.265}Gd_{0.735}F_{2.47}$, O′ is an F ion at the center of a cuboctahedron of F ions rather often encountered in the literature and mentioned in Ref. (*7*).

Conclusions

What we want to emphasize finally is that in the fluorite superstructures above, the cation lattice stays nearly invariant and that the origin O′ of the superstructure does not necessarily coincide with the origin of the fluorite structure, but coincides with a point of high site symmetry.

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