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Abnormal orientation variants and interfaces in ferroelastics and precautions to be taken for the use of group theory (example: rare earth sesquioxides)

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Abstract. — In group-subgroup phase transitions the orientation variants of the low symmetry structure are related by symmetry operations of the high symmetry structure which have been lost in the phase transition. In the case of the ferroelastic A (hexagonal) → B (monoclinic) phase transition of rare earth sesquioxides, orientation variants can occur which are not related by such symmetry operations but by the symmetry operations which would correspond to a twin (without change of the lattice) of the hexagonal structure. This phenomenon can occur when it reduces the high strain or high interface energies existing during the ferroelastic phase transition. Precautions necessary for the use of group theory in the study of ferroelastic orientation variants will be given. Special interest has also been taken in the study, by high resolution electron microscopy, of interfaces between a normal orientation variant and an unexpected (or abnormal) orientation variant. The interface has a certain thickness with possible atomic rearrangement.

1. Introduction.

In a previous paper [1] it has been shown that the A (hexagonal) → B (monoclinic) phase transition of rare earth sesquioxides is ferroelastic of the $\bar{3}m$ $F\ 2/m$ species of the Aizu classification [2] (see appendix I). It has also been shown by two of us [3, 4, 5] that small rotations between different orientation variants could greatly modify the domain structure of the ferroelastic phase. These observations did not however basically question the use of group theory for predicting the number and relative orientation of the different orientation variants. This theory has moreover been greatly used for rediscov-
problem about the use, as is usually done, of group theory for determination of the number and relative orientation of the different possible orientation variants. An analysis of this problem will be given here leading to precautions to be taken for the use of group theory in the study of ferroelastic orientation variants. A special interest is also taken in the study, by high resolution electron microscopy, of interfaces between normal and unexpected (abnormal) orientation variants.

2. Existence of unexpected (or abnormal) ferroelastic variants.

Determination of the number of orientation variants in a group-subgroup phase transition is based on the idea that the symmetry elements of the high symmetry structure, which are lost at the phase transition relate the different orientation variants of the low symmetry structure together. This is in perfect agreement with experiments in the case of a group subgroup phase transition if no deformation occurs. In the case of a ferroelastic phase transition which implies deformation of the lattice, small rotations, as previously shown [3, 4] must be taken into account. In the case of the monoclinic structure of Sm$_2$O$_3$ or Nd$_2$O$_3$ which are ferroelastic of the $\bar{3}$m F $2/m$ species it has moreover been shown [9] that orientation variants can be related by twins which do not correspond to symmetry elements of the high symmetry structure. These twins are the (111), (111), [192] and [192] twins of the monoclinic structure. They correspond to four equivalent symmetry operations which transform a crystal of the hexagonal structure in a possible merohedral twin. The existence of the merohedral twin in the hexagonal structure could then explain the existence of unexpected twins in the low symmetry structure. A twin has recently been identified in the hexagonal structure by electron microscopy [10]. This twin can be described by a rotation of $\pi$ about the three-fold axis or any equivalent symmetry operation. All these operations do not change the hexagonal lattice but in the same way change the orientation of the unit cell. The reciprocal lattice is unchanged so that the twin is a merohedral twin. Only the intensity of corresponding diffraction spots are modified so that the twin appears by electron microscopy with a weak contrast.

To the eight equivalent symmetry operations which relate the merohedral twinned crystals (appendix II) four correspond to the (111), (111), [192] and [192] twins of the monoclinic structure. The other four which are the (201), [101], (101) and [102] twins have not been observed. Because of the symmetry elements of the monoclinic structure the (201) and [102] twins are identical and also the (101) and [101] twins so that only two different twins have not been observed. The four twins which exist in the monoclinic structure being much more usual than the merohedral twin they cannot be due to the transformation of a twinned hexagonal crystal. The existence of these twins can only be due to a change of the orientation of the unit cell at the phase transformation itself. Such a phenomenon is unexpected because it needs energy to occur. It seems not to have been previously observed. In the case of B-Sm$_2$O$_3$ or B-Nd$_2$O$_3$ it could be related to the great deformation occurring at the transformation [1] so that a high strain energy results. The change of the orientation of the unit cell could then, in a rather complicated way, minimize the total free energy. Taking such a phenomenon into account the number of possible orientation variants $n$ is then the same as in the case of a 6/mmm F 2/m ferroelastic phase transition: $n = 24/4 = 6$ (appendix I). All these variants are observed. Interfaces are all the possible $W$ or $W'$ walls (strain free interfaces) between them. It must be noticed that some of these possible interfaces have not been observed which could be related to the way in which the corresponding orientation variants are created. It must also be noticed that six orientation variants being expected 5 $W$ and 5 $W'$ walls may occur. They are the (313), (3$\bar{1}$3) « (310)»-corresponding to the [192] twin-, « (310)»- corresponding to the [192] twin-, and finally the (101) and (201) planes which are at once W and $W'$ walls for respectively the (101) and [10$\bar{1}$] twins and for the (201) and [102] twins (see Table II, appendix II). $[\langle xyz\rangle]$ represents a plane which is not a reticular plane close to the (xyz) reticular one.

3. Mechanism of formation of abnormal orientation variants and precautions to be taken for the use of group theory.

Ferromagnetic ferroelectric and ferroelastic phase transitions are group-subgroup phase transitions with very similar characteristics. Small deformations can occur in the first two cases but it is the basic phenomenon only in ferroelastic phase transitions. This basic deformation is always related to a change of the lattice which is of a lower symmetry in the ferroelastic than in the prototypic structure. The importance of this deformation is related to the value of the coefficients of the spontaneous strain tensor. The importance of the strain energy when the prototypic and ferroelastic phases exist at once is obviously related to the value of these coefficients which are specially high in the case of the B phase of rare earth sesquioxides. Interfaces which are encountered between different orientation variants and between prototypic and ferroelastic variants are always strainfree showing the importance of strain energy at the transition. Moreover the ferroelastic
phase always grows epitaxially inside the prototypic phase \([3, 4]\). At the transformation the minimization of the total free energy finally occurs in a rather complicated way but two points appear to be most important:

i) the existence of only strainfree interfaces,
ii) the epitaxial growth of the ferroelastic phase on the prototypic one.

Because of the deformation this is only possible if the ferroelastic phase is made of twinned crystals. Multitwinned nuclei of the ferroelastic structure may then occur with abnormal twins and orientation variants. This is the first process of their formation: \(\langle 111 \rangle\) and \(\langle 192 \rangle\) twins can be encountered in such ferroelastic nuclei growing inside the hexagonal structure of rare earth sesquioxides (Fig. 1) where they reduce the strain energy \([4]\). Moreover the growth of the ferroelastic phase is a rather complicated phenomenon where interfaces between variants exactly related by a rotation of \(2\pi/3\) are equivalent to few degrees rotation—twin interfaces \([5]\). These interfaces are high energy interfaces and can dissociate into two twins as the two \(\langle 111 \rangle\) and \(\langle 192 \rangle\) twins of rare earth sesquioxides giving rise to a new domain of abnormal orientation (Fig. 2). This is a second possible mechanism for the formation of abnormal twins and orientation variants. In both cases their formation is related to a minimization of the total free energy by reduction of either the strain or the interface energy. In both cases it can be related to the fact that we deal with a ferroelastic phase transition with an important deformation related to a high value of the coefficients of the strain tensor.

The number of possible orientation variants, their relative orientation and the position of strainfree interfaces can then be deduced as if the transition were a group-subgroup phase transition, but between the holohedry of the high symmetry structure and the low symmetry structure. The transition behaves as a new ferroelastic species that must be used as soon as the orientation of the unit cell can change at the transition. This can only occur for species for which the high symmetry structure is not the holohedry itself. The case of the B structure of rare earth sesquioxides has shown that for the \(3\bar{m}\) point group the phenomenon may also occur and the holohedry of the rhombohedral structure behaves as a merihedry of the hexagonal structure so that the rhombohedral and hexagonal systems must be considered as the same one.

To the opposite of strainfree interfaces between two different normal orientation variants an interface between a normal and an abnormal one is such that the atomic vicinity of the interface is very far from the bulk, making these interfaces to be of a special interest.

![Fig. 1. — Formation of abnormal orientation variants: 1st mechanism. Multitwinned nuclei of monoclinic Sm2O3 (B) grow inside hexagonal structure (A). Twins are \(\langle 111 \rangle\) and \(\langle 192 \rangle\) twins (indicated W and W') giving rise to an abnormal orientation variant. Monoclinic and hexagonal regions are separated by interfaces indicated I.](image1)

![Fig. 2. — Formation of abnormal orientation variants: 2nd mechanism. A \(2\pi/3\) rotation interface (R) dissociates into two \(\langle 111 \rangle\) and \(\langle 192 \rangle\) twins (W and W') giving rise to an abnormal orientation variant (a mechanism of the formation of rotation interfaces can be found in reference \([5]\)).](image2)

4. High resolution electron microscopy study of unexpected interfaces.

Normal orientation variants are related by symmetry operations which correspond to symmetry elements of the hexagonal crystals (they are pseudo-symmetry elements of the monoclinic crystal). Abnormal orientation variants are related by symmetry operations which only correspond to symmetry elements of the hexagonal lattice (they are pseudo-symmetry elements of the monoclinic lattice). This is obviously due to the fact that normal orientation variants are
obtained by transition of the $\overline{3}m$ $F \overline{2}/m$ species while abnormal orientation variants should be obtained by transition of the $6/mmm$ $F \overline{2}/m$ species (where orientation variants obtained by the transition of the $\overline{3}m$ $F \overline{2}/m$ species are eliminated). Normal and abnormal interfaces are then very different. In the case of W interfaces for example, the interface is a mirror plane which in the first case is a pseudosymmetry plane of the monoclinic structure and in the second case is only a pseudosymmetry plane of the monoclinic lattice. The atomic misfit at the interface is very different in each case and much more serious in the second case.

As previously shown [11], W walls between two of the three normal $E_1$, $E_2$, $E_3$ orientation variants of the B structure of rare earth sesquioxides (which are $\{313\}$ twins) have perfectly defined planar interfaces without any thickness and without atomic rearrangement (Fig. 3). To the contrast, W walls between for example $E_1$ and $E_4$, $E_5$ or $E_6$ variants (appendix I) which are abnormal interfaces, as for example the $\{111\}$ twins of rare earth sesquioxides, have a certain thickness by H.R.E.M. imaging (Fig. 4) when the electron beam is parallel to the $[10\overline{1}]$ axis.

The high resolution image is obtained by using the direct electron beam and the $[111]$, $\overline{1}1\overline{1}$, $\overline{1}1\overline{1}$, $\overline{1}1\overline{1}$, $102$, $202$ diffracted beams. The origin of the thickness of the image of the interface is not completely elucidated. It could be due to some inclination of the interface related to the $\{111\}$ plane but since the apparent thickness is always nearly exactly three reticular distances ($\approx 1\,\text{nm}$), a simple tilt of the interface seems to be so far (and before image computation) irrelevant with experiment. The apparent thickness is more likely due some atomic rearrangement occurring in the vicinity of the interface itself related to a very bad local atomic misfit at the interface. Rare earth atoms as well as oxygen atoms are too close at the interface. No model of a possible atomic rearrangement that could fit in with experimental images is until now available.

5. Conclusion.

It has been shown that the orientation of the unit cell can be changed in a ferroelastic phase transition if the prototypic structure is not the holohedry of the crystalline system (rhombohedral and hexagonal systems must be considered as the same one). Then the ferroelastic transition behaves like a transition between the holohedry corresponding to the high symmetry structure and the low symmetry structure. This defines a new ferroelastic species, giving rise to unexpected (or abnormal) orientation variants. Unexpected strainfree interfaces can also exist. Group theory used for the determination of the number and relative orientation of orientation variants and of strainfree interfaces must finally be done as in the case of a ferroelastic species between the holohedry of the high symmetry structure and the low symmetry structure. The H.R.E.M. image of abnormal interfaces show a certain thickness at the interface that can be related to a possible atomic rearrangement due to a very bad local atomic misfit.

Appendix I.

Point Group Representation of the Hexagonal (A)-Monoclinic (B) Transition of Rare Earth Sesquioxides. — The transition is of the $\overline{3}m$ $F \overline{2}/m$ species but it sometimes behaves as if it were of $6/mmm$ $F \overline{2}/m(s)$ species.

I.1 Transition of the $\overline{3}m$ $F \overline{2}/m$ Species. — The symmetry elements of the ferroelastic structure are:

- at twofold axis along the $b$ axis: $2[010]$,
- a mirror plane parallel to the $(010)$ plane: $m_{(010)}$, and
- the inversion $i$ about inversion centres located at the origin and at $\frac{1}{2}, \frac{1}{2}, 0$ (base centred structure).
The symmetry elements of the prototypic structure are the same plus $2\pi/3$ and $4\pi/3$ rotations about the threefold axis $(3^1, 3^2)$ or any equivalent operation. Different possible variants of rotation domains of the low symmetry structure can be deduced by a decomposition of the point-group of high symmetry; it can be written in the following way:

$$\{\tilde{3}m\} = \left\{ \frac{2}{m} \right\} (1) + \left\{ \frac{2}{m} \right\} (3^1) + \left\{ \frac{2}{m} \right\} (3^2).$$

The three operations indicated by $(1)$ $(3^1)$, and $(3^2)$ respectively fit in with the rotation of $2\pi$, $2\pi/3$ and $4\pi/3$ about the [001] axis of A. We denote the corresponding domains $E_1$, $E_2$, $E_3$ respectively.

1.2 TRANSITION OF THE $6/mmm$ F $2/m(s)$ SPECIES. — In the same way, different possible rotation variants of the low symmetry structure of this species can be deduced by a decomposition of the point group of the high symmetry structure. It can be written in the following way:

$$\{\text{6 m mm} \} = \left\{ \frac{2}{m} \right\} (1) + (6^1) + (6^2) + (6^3) + (6^4).$$

The other three operations indicated by $(1)$ $(6^2)$ and $(6^3)$ respectively fit in with a rotation of $2\pi$, $2\pi/3$ and $2\pi/3$ about the [001] axis of A. Domains related by these operations are found by the $3m$ F $2m$ decomposition $(3m$ is a subgroup of $6/mmm)$: $E_4$, $E_5$, $E_6$. The other three operations indicated by $(6^1)$, $(6^2)$ and $(6^3)$ respectively fit in with a rotation of $\pi/3$, $\pi$ and $-\pi/3$ about the [001] axis of A. We denote the corresponding domains: $E_4$, $E_5$, $E_6$ respectively. These domains are not deduced by the $3m$ F $2m$ decomposition.

Appendix II.

INTERFACES BETWEEN ORIENTATION VARIANTS OF MONOCLINIC (B) RARE EARTH SESQUIOXIDES. — One of the orientation variants (1) of the ferroelastic structure (B) of rare earth sesquioxides can be characterized by the spontaneous strain tensor $S$ (from [2]), which corresponds to the pure deformation from the prototypic to the ferroelastic structure

$$S = \begin{bmatrix} p & 0 & q \\ 0 & -p & 0 \\ q & 0 & 0 \end{bmatrix}. \quad (1)$$

Possible change in volume being taken off this tensor is traceless.

Values of $p$ and $q$ for B are $42.5 \times 10^{-3}$ and $30.0 \times 10^{-3}$ respectively (from [1]) which are specially high values. The other orientation variants (2) and (3) are characterized by spontaneous strain tensors $S'$ such that

$$S' = (\alpha) S (\alpha)^{-1}, \quad (2)$$

where $\alpha$ is the transformation matrix from domain (1) to domain (2) or (3). All these tensors are given in an orthogonal system of basic vectors $I, J, K$ such that $|I| = |J| = |K| = 1$ and related to the basic vectors of the prototypic hexagonal structure (A): $a, b, c$ by relation (3):

$$\begin{bmatrix} a \\ b \\ c \end{bmatrix} = \begin{bmatrix} 0 & -a & 0 \\ a \sqrt{3}/2 & a/2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} I \\ J \\ K \end{bmatrix}. \quad (3)$$

The basic vectors $a_m, b_m, c_m$ of the monoclinic structure are related to $a, b, c$ by relation (4):

$$\begin{bmatrix} a_m \\ b_m \\ c_m \end{bmatrix} = \begin{bmatrix} 1 & 2 & 2 \\ 1 & 0 & 0 \\ 1 & 2 & 1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}. \quad (4)$$

Interfaces between orientation variants are such that no long range strain exists on either side of the interfaces. This occurs if the spontaneous strain is the same on each side of the interface for the two different orientation variants. This condition is satisfied by:

$$S_{ij} - S'_{ij} x_i x_j = 0, \quad (5)$$

where $S$ and $S'$ are the two spontaneous strain tensors of the two neighbouring variants. The solution of equation (5) is a cone of apex 0 origin of the orthogonal system taken at the interface. It is physically acceptable only if this cone has no special point i.e. if it is dissociated into two planes which occurs if:

$$\det |S - S'| = 0, \quad (6)$$

tensors being traceless, the two planes are perpendicular.

Some of the possible strainfree interfaces can be entirely determined by symmetry considerations. If two orientation variants are related by a mirror operation (type I twin) planes parallel to the mirror are possible interfaces. They are then crystallographic planes and are indicated W. Other possible interfaces cannot be determined by symmetry considerations. If two orientation variants are related by rotation of $\pi$ about an axis (type II twin) the corresponding strainfree interface deduced from (5) is a plane containing the twinning axis. It is indicated $W'$. It is generally not a crystallographic plane, but in the case of the B structure the $W'$ wall associated with the $[10\overline{1}]$ twin is the $(101)$ plane and the $W'$ wall associated with the $[102]$ twin is the $(201)$ plane. It must be noticed that this classification
in W and W' walls is (out of small rotations not taken into account here), equivalent to the classification in twins of type I and type II.

Let us now calculate the possible strainfree interfaces of the A-B transition considered first as of the \( \bar{3}m \) F 2/m species and then as being of the 6/mmm F 2/m(s) species.

1) Strainfree interfaces of the \( \bar{3}m \) F 2/m species. — The phase transition gives rise to three different orientation variants \( E_1, E_2, E_3 \) corresponding to (1) (3') , (3'). Strainfree interfaces between different variants are solutions of equations (5) and (6) given in the orthogonal system. These interfaces are shown in table I by their Miller indices in the orthogonal, hexagonal and monoclinic systems.

<table>
<thead>
<tr>
<th>Reference system</th>
<th>(O, I, J, K)</th>
<th>(O, a, b, c)</th>
<th>(O, a_m, b_m, c_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Miller indices</strong></td>
<td>HKL</td>
<td>hkl</td>
<td>( h_m k_m l_m )</td>
</tr>
<tr>
<td>( W_{12} )</td>
<td>( \sqrt[3]{310} )</td>
<td>( \bar{12}0 )</td>
<td>( \bar{313} )</td>
</tr>
<tr>
<td>( W_{12} )</td>
<td>( \rho, -\rho, \sqrt[3]{3}, 2 q ) ( a\sqrt[3]{3}, 0, 2 q )</td>
<td>( \approx ) ( \sqrt[3]{3}0 )</td>
<td></td>
</tr>
<tr>
<td>( W_{13} )</td>
<td>( \sqrt[3]{310} )</td>
<td>( 11.0 )</td>
<td>( \bar{313} )</td>
</tr>
<tr>
<td>( W_{13} )</td>
<td>( \rho, \rho, \sqrt[3]{3}, 2 q ) ( -a\sqrt[3]{3}, a\sqrt[3]{3}, 2 q )</td>
<td>( \approx ) ( \sqrt[3]{3}0 )</td>
<td></td>
</tr>
</tbody>
</table>

It is clear that the (313) twin of B corresponds to the (110) symmetry plane of A and that the (313) twin of B corresponds to the (110) symmetry plane of A. The \( \{310\} W' \) wall correspond to the [132] twin and the \( \{310\} W' \) wall to the [132] twin. These two twins correspond to two of the \( \{110\} \) symmetry axes of the hexagonal structure.

2) Strainfree interfaces of the 6/mmm F 2/m(s) species. — The phase transition gives rise to six different orientation variants \( E_1, E_2, E_3, E_4, E_5, E_6 \) corresponding to (1) (3'), (3'), (6'), (6'), (6'). \( E_1, E_2, E_3 \) are the same as in the previous case and are related by the same strainfree interfaces. Interfaces between \( E_4, E_5 \) are similar, but interfaces between domains \( E_i (i = 1, 2, 3) \) and \( E_j (j = 4, 5, 6) \) are different. They are given for \( l = 1 \) in table II. Similar results should be obtained for \( l = 2, 3 \). It is clear that the (111) twin of B corresponds to the (100) symmetry plane of the hexagonal lattice (and twin plane of the hexagonal structure) and the (111) twin of B to the (110) symmetry plane of the hexagonal lattice. The \( \{1223\} \) \( W' \) wall corresponds to the [192] twin and the \( \{1223\} \) \( W' \) wall to the [192] twin. These two twins correspond to two of the \( \{100\} \) symmetry axes of the hexagonal lattice. Two other possible interfaces: (101) and (201) which are at once W and W' walls have not been encountered.

Table I. — Indices of interfaces between domains (1), (2) and (1), (3).

<table>
<thead>
<tr>
<th>Reference system</th>
<th>(O, I, J, K)</th>
<th>(O, a, b, c)</th>
<th>(O, a_m, b_m, c_m)</th>
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</thead>
<tbody>
<tr>
<td><strong>Miller indices</strong></td>
<td>HKL</td>
<td>hkl</td>
<td>( h_m k_m l_m )</td>
</tr>
<tr>
<td>( W_{(1) - (4)} )</td>
<td>(1, ( \sqrt[3]{3} ), 0)</td>
<td>( \bar{11}0 )</td>
<td>( {111} )</td>
</tr>
<tr>
<td>( W_{(1) - (4)} )</td>
<td>( \frac{3}{2} \rho, \frac{\sqrt[3]{3}}{2} \rho, -q )</td>
<td>( \frac{\sqrt[3]{3}}{2} ap, -\frac{\sqrt[3]{3}}{2} aq, -cq )</td>
<td>( \approx ) ( {12, 2, 3} )</td>
</tr>
<tr>
<td>( W_{(1) - (5)} )</td>
<td>(100)</td>
<td>(010)</td>
<td>(202)</td>
</tr>
<tr>
<td>( W_{(1) - (5)} )</td>
<td>(001)</td>
<td>(001)</td>
<td>(201)</td>
</tr>
<tr>
<td>( W_{(1) - (6)} )</td>
<td>(( \bar{1}, \sqrt[3]{3} ), 0)</td>
<td>( \frac{\sqrt[3]{3}}{2} \rho, \sqrt[3]{3} \rho, q )</td>
<td>( \frac{\sqrt[3]{3}}{2} ap, \sqrt[3]{3} ap, cq )</td>
</tr>
</tbody>
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References