

1. SPACE GROUPS AND THEIR SUBGROUPS

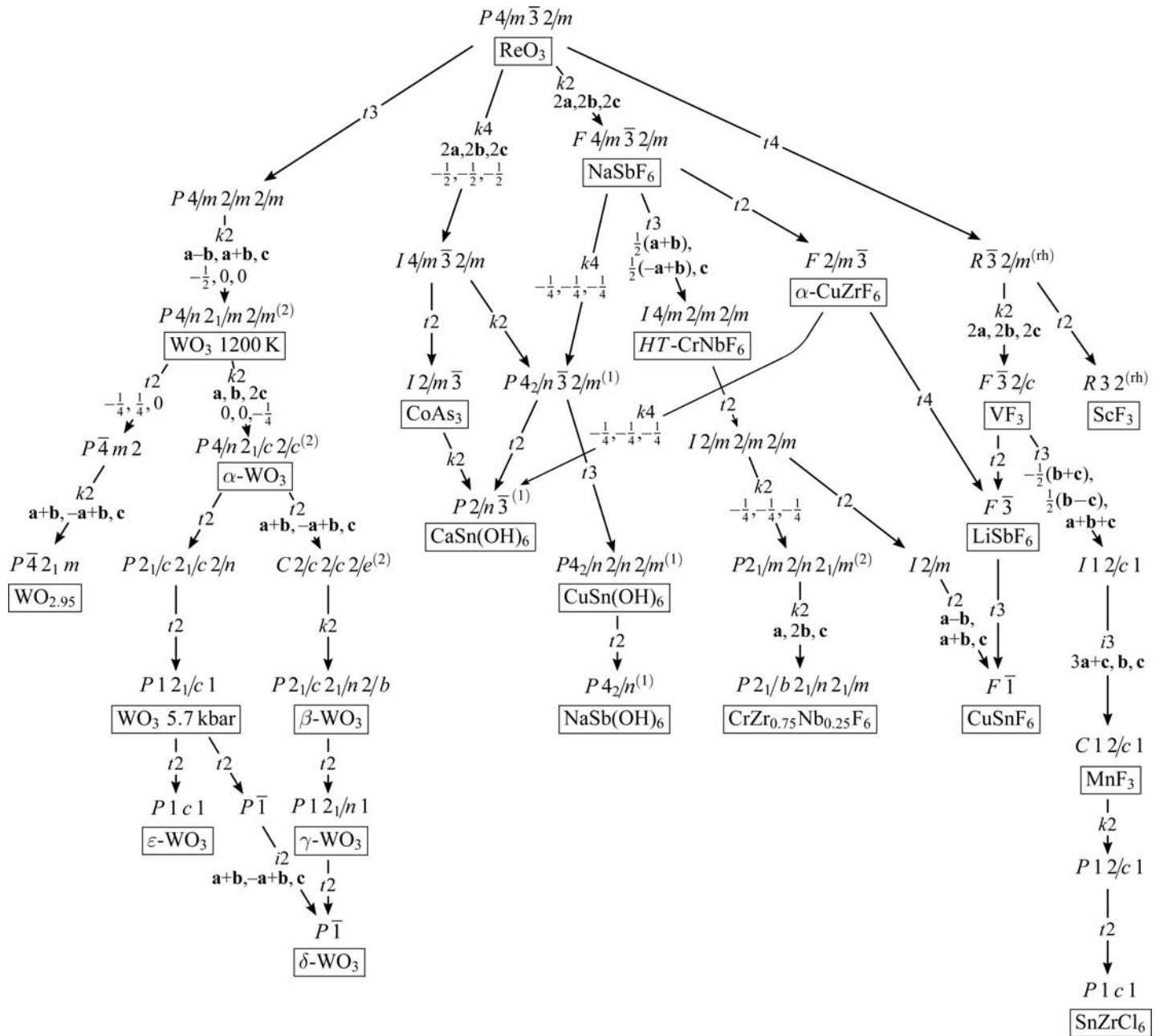


Fig. 1.6.4.10. Bärnighausen tree of hettotypes of the ReO_3 type. For the atomic parameters and other crystallographic data see Bock & Müller (2002b). $F\bar{3}2/c$ and $F\bar{3}$ are nonconventional face-centred settings of $R\bar{3}2/c$ and $R\bar{3}$, respectively, with rhombohedral-axes setting and nearly cubic metric, $F\bar{1}$ is a nearly cubic setting of $P\bar{1}$. Every space-group symbol corresponds to one space group (not space-group type) belonging to a specific crystal structure. Note that the vertical distances between space-group symbols are proportional to the logarithms of the indices.

(Müller, 1986), wurtzite derivatives (Baur & McLarnan, 1982) and NaCl derivatives with doubled cell (Sens & Müller, 2003).

1.6.5. Handling cell transformations

It is important to keep track of the coordinate transformations in a sequence of group–subgroup relations. A Bärnighausen tree can only be correct if every atomic position of every hettotype can be derived from the corresponding positions of the aristotype. The mathematical tools are described in Sections 1.2.2.3, 1.2.2.4 and 1.2.2.7 of this volume and in Part 5 of Volume A.

A basis transformation and an origin shift are mentioned in the middle of a group–subgroup arrow. This is a shorthand notation for the matrix–column pair (Seitz symbol; Section 1.2.2.3) or the 4×4 matrix (augmented matrix, Section 1.2.2.4) to be used to calculate the basis vectors, origin shift and coordinates

of a maximal subgroup from those of the preceding space group. If there is a sequence of several transformations, the overall changes can be calculated by multiplication of the 4×4 matrices.

Let P_1, P_2, \dots be the 4×4 matrices expressing the basis vector and origin changes of several consecutive cell transformations. $P_1^{-1}, P_2^{-1}, \dots$ are the corresponding inverse matrices. Let $\mathbf{a}, \mathbf{b}, \mathbf{c}$ be the starting (old) basis vectors and $\mathbf{a}', \mathbf{b}', \mathbf{c}'$ be the (new) basis vectors after the consecutive transformations. Let \mathbf{x} and \mathbf{x}' be the augmented columns of the atomic coordinates before and after the transformations. Then the following relations hold:

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}', \mathbf{p}) = (\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{o}) P_1 P_2, \dots \quad \text{and} \quad \mathbf{x}' = \dots P_2^{-1} P_1^{-1} \mathbf{x}.$$

\mathbf{p} is the vector of the origin shift, i.e. its components are the coordinates of the origin of the new cell expressed in the coord-

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dinate system of the old cell; \mathbf{o} is a zero vector. Note that the inverse matrices have to be multiplied in the reverse order.

Example 1.6.5.1

Take a transformation from a cubic to a rhombohedral unit cell (hexagonal setting) combined with an origin shift of $\mathbf{p}_1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ (in the cubic coordinate system), followed by transformation to a monoclinic cell with a second origin shift of $\mathbf{p}_2 = (-\frac{1}{2}, -\frac{1}{2}, 0)$ (in the hexagonal coordinate system). From Fig. 1.6.5.1 (left) we can deduce

$$\mathbf{a}_{\text{hx}} = \mathbf{a}_{\text{cb}} - \mathbf{b}_{\text{cb}}, \quad \mathbf{b}_{\text{hx}} = \mathbf{b}_{\text{cb}} - \mathbf{c}_{\text{cb}}, \quad \mathbf{c}_{\text{hx}} = \mathbf{a}_{\text{cb}} + \mathbf{b}_{\text{cb}} + \mathbf{c}_{\text{cb}},$$

which in matrix notation is

$$\begin{aligned} (\mathbf{a}_{\text{hx}}, \mathbf{b}_{\text{hx}}, \mathbf{c}_{\text{hx}}) &= (\mathbf{a}_{\text{cb}}, \mathbf{b}_{\text{cb}}, \mathbf{c}_{\text{cb}}) \mathbf{P}_1 \\ &= (\mathbf{a}_{\text{cb}}, \mathbf{b}_{\text{cb}}, \mathbf{c}_{\text{cb}}) \begin{pmatrix} 1 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}. \end{aligned}$$

In the fourth column of the 4×4 matrix \mathbb{P}_1 we include the components of the origin shift, $\mathbf{p}_1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$:

$$\mathbb{P}_1 = \left(\begin{array}{ccc|c} \mathbf{P}_1 & \mathbf{p}_1 \\ \mathbf{o} & 1 \end{array} \right) = \left(\begin{array}{ccc|c} 1 & 0 & 1 & \frac{1}{4} \\ -1 & 1 & 1 & \frac{1}{4} \\ 0 & -1 & 1 & \frac{1}{4} \\ \hline 0 & 0 & 0 & 1 \end{array} \right).$$

The inverse matrix \mathbf{P}_1^{-1} can be calculated by matrix inversion, but it is more straightforward to deduce it from Fig. 1.6.5.1; it is the matrix that converts the hexagonal basis vectors back to the cubic basis vectors:

$$\begin{aligned} \mathbf{a}_{\text{cb}} &= \frac{2}{3}\mathbf{a}_{\text{hx}} + \frac{1}{3}\mathbf{b}_{\text{hx}} + \frac{1}{3}\mathbf{c}_{\text{hx}}, & \mathbf{b}_{\text{cb}} &= -\frac{1}{3}\mathbf{a}_{\text{hx}} + \frac{1}{3}\mathbf{b}_{\text{hx}} + \frac{1}{3}\mathbf{c}_{\text{hx}}, \\ \mathbf{c}_{\text{cb}} &= -\frac{1}{3}\mathbf{a}_{\text{hx}} - \frac{2}{3}\mathbf{b}_{\text{hx}} + \frac{1}{3}\mathbf{c}_{\text{hx}}, \end{aligned}$$

$$\begin{aligned} (\mathbf{a}_{\text{cb}}, \mathbf{b}_{\text{cb}}, \mathbf{c}_{\text{cb}}) &= (\mathbf{a}_{\text{hx}}, \mathbf{b}_{\text{hx}}, \mathbf{c}_{\text{hx}}) \mathbf{P}_1^{-1} \\ &= (\mathbf{a}_{\text{hx}}, \mathbf{b}_{\text{hx}}, \mathbf{c}_{\text{hx}}) \begin{pmatrix} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix}. \end{aligned}$$

The column part (fourth column) of the inverse matrix \mathbb{P}_1^{-1} is $-\mathbf{P}_1^{-1}\mathbf{p}_1$ (cf. equation 1.2.2.6):

$$-\mathbf{P}_1^{-1}\mathbf{p}_1 = -\begin{pmatrix} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} \begin{pmatrix} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ -\frac{1}{4} \end{pmatrix}.$$

Therefore, \mathbb{P}_1^{-1} is

$$\mathbb{P}_1^{-1} = \left(\begin{array}{ccc|c} \mathbf{P}_1^{-1} & -\mathbf{P}_1^{-1}\mathbf{p}_1 \\ \mathbf{o} & 1 \end{array} \right) = \left(\begin{array}{ccc|c} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} & -\frac{1}{4} \\ \hline 0 & 0 & 0 & 1 \end{array} \right).$$

Similarly, for the second (hexagonal to monoclinic) transformation, we deduce the matrices $\mathbf{P}_2, \mathbf{P}_2^{-1}$ and the column part of $\mathbb{P}_2^{-1}, -\mathbf{P}_2^{-1}\mathbf{p}_2$, from the right image of Fig. 1.6.5.1:

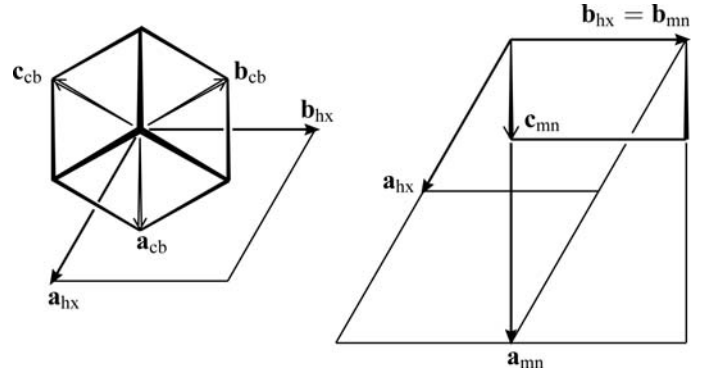


Fig. 1.6.5.1. Relative orientations of a cubic to a rhombohedral cell (hexagonal setting) (left) and of a rhombohedral cell (hexagonal setting) to a monoclinic cell (the monoclinic cell has an acute angle β).

$$\begin{aligned} (\mathbf{a}_{\text{mn}}, \mathbf{b}_{\text{mn}}, \mathbf{c}_{\text{mn}}) &= (\mathbf{a}_{\text{hx}}, \mathbf{b}_{\text{hx}}, \mathbf{c}_{\text{hx}}) \mathbf{P}_2 \\ &= (\mathbf{a}_{\text{hx}}, \mathbf{b}_{\text{hx}}, \mathbf{c}_{\text{hx}}) \begin{pmatrix} 2 & 0 & \frac{2}{3} \\ 1 & 1 & \frac{1}{3} \\ 0 & 0 & \frac{1}{3} \end{pmatrix} \\ (\mathbf{a}_{\text{hx}}, \mathbf{b}_{\text{hx}}, \mathbf{c}_{\text{hx}}) &= (\mathbf{a}_{\text{mn}}, \mathbf{b}_{\text{mn}}, \mathbf{c}_{\text{mn}}) \mathbf{P}_2^{-1} \\ &= (\mathbf{a}_{\text{mn}}, \mathbf{b}_{\text{mn}}, \mathbf{c}_{\text{mn}}) \begin{pmatrix} \frac{1}{2} & 0 & -1 \\ -\frac{1}{2} & 1 & 0 \\ 0 & 0 & 3 \end{pmatrix} \\ -\mathbf{P}_2^{-1}\mathbf{p}_2 &= -\begin{pmatrix} \frac{1}{2} & 0 & -1 \\ -\frac{1}{2} & 1 & 0 \\ 0 & 0 & 3 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} \\ -\frac{1}{2} \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{4} \\ \frac{1}{4} \\ 0 \end{pmatrix}. \end{aligned}$$

For the basis vectors of the two consecutive transformations we calculate:

$$\begin{aligned} \mathbb{P}_1\mathbb{P}_2 &= \left(\begin{array}{ccc|c} 1 & 0 & 1 & \frac{1}{4} \\ -1 & 1 & 1 & \frac{1}{4} \\ 0 & -1 & 1 & \frac{1}{4} \\ \hline 0 & 0 & 0 & 1 \end{array} \right) \left(\begin{array}{ccc|c} 2 & 0 & \frac{2}{3} & -\frac{1}{2} \\ 1 & 1 & \frac{1}{3} & -\frac{1}{2} \\ 0 & 0 & \frac{1}{3} & 0 \\ \hline 0 & 0 & 0 & 1 \end{array} \right) \\ &= \left(\begin{array}{ccc|c} 2 & 0 & 1 & -\frac{1}{4} \\ -1 & 1 & 0 & \frac{1}{4} \\ -1 & -1 & 0 & \frac{3}{4} \\ \hline 0 & 0 & 0 & 1 \end{array} \right), \end{aligned}$$

$$\begin{aligned} (\mathbf{a}_{\text{mn}}, \mathbf{b}_{\text{mn}}, \mathbf{c}_{\text{mn}}, \mathbf{p}) &= (\mathbf{a}_{\text{cb}}, \mathbf{b}_{\text{cb}}, \mathbf{c}_{\text{cb}}, \mathbf{o}) \mathbb{P}_1\mathbb{P}_2 \\ &= (\mathbf{a}_{\text{cb}}, \mathbf{b}_{\text{cb}}, \mathbf{c}_{\text{cb}}, \mathbf{o}) \left(\begin{array}{ccc|c} 2 & 0 & 1 & -\frac{1}{4} \\ -1 & 1 & 0 & \frac{1}{4} \\ -1 & -1 & 0 & \frac{3}{4} \\ \hline 0 & 0 & 0 & 1 \end{array} \right), \end{aligned}$$

which corresponds to

$$\mathbf{a}_{\text{mn}} = 2\mathbf{a}_{\text{cb}} - \mathbf{b}_{\text{cb}} - \mathbf{c}_{\text{cb}}, \quad \mathbf{b}_{\text{mn}} = \mathbf{b}_{\text{cb}} - \mathbf{c}_{\text{cb}}, \quad \mathbf{c}_{\text{mn}} = \mathbf{a}_{\text{cb}}$$

and an origin shift of $\mathbf{p} = (-\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$ in the cubic coordinate system. The corresponding (cubic to monoclinic) coordinate transformations result from

$$\begin{aligned} \mathbf{x}_{mn} &= \mathbb{P}_2^{-1} \mathbb{P}_1^{-1} \mathbf{x}_{cb} \\ \begin{pmatrix} x_{mn} \\ y_{mn} \\ z_{mn} \\ 1 \end{pmatrix} &= \begin{pmatrix} \frac{1}{2} & 0 & -1 & \frac{1}{4} \\ -\frac{1}{2} & 1 & 0 & \frac{1}{4} \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} & -\frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_{cb} \\ y_{cb} \\ z_{cb} \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} 0 & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 0 & \frac{1}{2} & -\frac{1}{2} & \frac{1}{4} \\ 1 & 1 & 1 & -\frac{3}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_{cb} \\ y_{cb} \\ z_{cb} \\ 1 \end{pmatrix}, \end{aligned}$$

which is the same as

$$\begin{aligned} x_{mn} &= -\frac{1}{2}y_{cb} - \frac{1}{2}z_{cb} + \frac{1}{2}, & y_{mn} &= \frac{1}{2}y_{cb} - \frac{1}{2}z_{cb} + \frac{1}{4}, \\ z_{mn} &= x_{cb} + y_{cb} + z_{cb} - \frac{3}{4}. \end{aligned}$$

1.6.6. Comments concerning phase transitions and twin domains

When a compound forms several polymorphic forms, a Bärnighausen tree can serve to show whether second-order phase transitions are feasible between them and what kinds of twin domains may be formed during such a transition. The possible kinds of domains can also be deduced for first-order phase transitions involving a group–subgroup relation and for topotactic reactions.

Second-order (continuous) phase transitions are only possible if there is a direct (not necessarily maximal) group–subgroup relation between the space groups of the two phases. If there is no such relation, for example, if two polymorphic forms can be related only by a common supergroup, the phase transformation can only be of first order. The condition of a direct group–subgroup relation is a necessary but not a sufficient condition; the phase transition can still be of first order.

The domain structure of crystalline phases that often results at solid-state phase transitions and during topotactic reactions can be transparently interpreted with the aid of symmetry considerations (Section 1.2.7; Bärnighausen, 1980; Janovec & Přívratská, 2003; van Tendeloo & Amelinckx, 1974; Wondratschek & Jeitschko, 1976). A domain structure is the result of nucleation and growth processes. The orientational relations between the phases before and after the transformation, as a rule, are not the result of a homogeneous process involving a simultaneous motion of the atoms in a single crystal. The crystalline matrix of the substrate rather governs the preferred orientation adopted by the nuclei that are formed during the course of the nucleation process. The crystallites that result from the subsequent growth of the nuclei maintain their orientations. Under these circumstances, aspect 3 of the symmetry principle, as stated in Section 1.6.2, is fully effective. A phase transition that is connected with a symmetry reduction will result in new phases that consist of

- (i) *twin domains* if the formed phase belongs to a crystal class with reduced symmetry, or
- (ii) *antiphase domains* (translational domains) if translational symmetry is lost.

The total number of domains, of course, depends on the number of nucleation sites. The number of different domain kinds, however, is ruled by the index of the symmetry reduction. At a *translationengleiche* symmetry reduction of index 3 (*t*3

group–subgroup relation) we can expect twins with three kinds of domains, having three different orientations. An isomorphic subgroup of index 5 (*i*5 relation), since it is a *klassengleiche* symmetry reduction, will entail five kinds of antiphase domains. If the symmetry reduction includes several steps (in a chain of several maximal subgroups), the domain structure will become more complicated. With two *t*2 group–subgroup relations, we can expect twins of twins with two kinds of domains each. In the example of Fig. 1.2.7.1, we have a sequence of one *t*2 and one *k*2 step; therefore, as explained in a more rigorous manner in Example 1.2.7.3.4, we can expect two kinds of twin domains having two different orientations and, in addition, two kinds of antiphase domains. The actual number of observable domain kinds may be less than expected if a domain kind is not formed during nucleation. This can be controlled by the nucleation conditions; for example, an external electric field can suppress the formation of more than one kind of differently oriented ferroelectric domains.

In the physical literature, phase transitions between *translationengleiche* space groups are sometimes called *ferroic* transitions, those between *klassengleiche* space groups are *non-ferroic*.

As mentioned at the end of Section 1.6.4.5, a common subgroup of two space groups usually is not suitable for relating two crystal structures. Just so, a common crystallographic subgroup is unfit to explain the mechanism for a reconstructive, first-order phase transition. Such mechanisms have been proposed repeatedly (see, e.g., Capillas *et al.*, 2007, and references therein). Like in a second-order transition, continuous atomic movements have been assumed, leading first to a structure with the reduced symmetry of a common subgroup, followed by a symmetry increase to the space group of the second phase. However, a first-order transition always shows hysteresis, which means that the initial and the final phase coexist during the transition and that there is a phase boundary between them. The transition begins at a nucleation site, followed by the growth of the nucleus (see, e.g., Binder, 1987; Chaitkin & Lubensky, 1995; Chandra Shekar & Gavinda Rajan, 2001; Christian, 2002; Doherty, 1996; Gunton, 1984; Herbststein, 2006; Jena & Chaturvedi, 1992; Wayman & Bhadeshia, 1996). The reconstruction of the structure and the necessary atomic motions occur at the phase boundary between the receding old phase and the growing new phase. Any intermediate state is restricted to this interface between the two phases. *It is impossible to assign a three-dimensional space group to an interface.* In addition, while the interface advances through the crystal, the atoms at the interface do not linger in a static state. A space group can only be assigned to a static state (time-dependent phenomena are not covered by space-group theory).

1.6.7. Exercising care in the use of group–subgroup relations

Using the tables of this volume or from other sources or using computer programs as offered by the Bilbao Crystallographic Server (see Chapter 1.7), it may be easy to search for group–subgroup relations between space groups of crystal structures. This should only be done bearing in mind and explicitly stating a crystallographic, physical or chemical context. It is senseless to construct relations in a purely formal manner, ‘just for fun’, without a sound crystal-chemical or physical foundation. There exist no clear criteria to determine what is a ‘sound foundation’, but crystallographic, chemical and physical common sense and knowledge should always be taken into consideration.