

1. SPACE GROUPS AND THEIR SUBGROUPS

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

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 & Přívratká, 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.