

3. SYMMETRY ASPECTS OF PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

normal to the twin mirror plane ($10\bar{1}0$) (cf. Klapper *et al.*, 1987). The short term ‘twin plane’ should be avoided in such cases and substituted by *twin mirror plane* or *twin reflection plane*. The frequently used term ‘twinning on (hkl) ’ [German: ‘Zwillinge nach (hkl) ’] refers to (hkl) as a twin mirror plane and not as a contact plane.

(6) There exist twins in which the twin operations can be regarded as *fivefold* or *tenfold* rotations (Ellner & Burkhardt, 1993; Ellner, 1995). These twins are due to pseudo-pentagonal or pseudo-decagonal metrical features of the lattice [$\gamma = \arctan(c/a) \approx 72^\circ$]. They can be treated in the same way as the three-, four- and sixfold rotation twins mentioned in Section 3.3.2.3.2. This includes the alternative (‘exact’) description of the twinning by a cyclic sequence of symmetry-equivalent twin reflection planes or twofold twin axes (cf. aragonite, Fig. 3.3.2.4). For this reason, we recommend that these intergrowths are accepted as (pseudo) n -fold rotation twins, even though the value of n is noncrystallographic.

(7) The classical treatment of twins considers only rotations, reflections and inversions as twin operations. In domain structures, relations between domain states exist that involve only *translations* (cf. Section 3.4.3), specifically those that are suppressed during a phase transition. Since every domain structure can be considered as a transformation twin, it seems legitimate to accept these translations as twin operations and speak of *translation twins* (T-twins according to Wadhawan, 1997, 2000). The translation vector of this twin operation is also known as the *fault vector* of the *translation boundary* (often called the *anti-phase boundary*) between two *translation domains* [cf. Section 3.3.1(v)]. It must be realized, however, that the acceptance of translation domains as twins would classify all stacking faults in metals, in diamond and in semiconductors as twin boundaries.

(8) The structural consideration of twin boundaries cannot be performed by employing only point-group twin elements as is sufficient for the description of the orientation relation. In structural discussions, in addition, a possible translational displacement of the two structures with respect to each other by a shift vector, which is called here the *twin displacement vector* \mathbf{t} , has to be taken into account. This displacement vector leads to a minimization of the twin-boundary energy. The components of this vector can have values between 0 and 1 of the basis vectors. In many cases, especially of transformation twins, glide planes or screw axes can occur as twin elements, whereby the glide or screw components may be relaxed, *i.e.* may deviate from their ideal values. The twin displacement vectors, as introduced here, include these glide or screw components as well as their relaxations. The role of the twin displacement vectors in the structure of the twin boundary is discussed in Section 3.3.10.4.

(9) In some cases the term ‘twin’ is used for systematic *oriented intergrowths* of crystals which are not twins as defined in this chapter. The following cases should be mentioned:

(i) *Allotwins* (Nespolo, Kogure & Ferraris, 1999): oriented crystal associations of different polytypes of the same compound. Different polytypes have the same chemistry and similar but nevertheless different structures. Well known examples are the micas, where twins and allotwins occur together (Nespolo *et al.*, 2000).

(ii) The oriented associations of two *polymorphs* (modifications) of the same compound across a phase boundary also do not deserve the name twin because of the different structures of their components. They are often called ‘syntaxy’. Note that this case is more general than the ‘allotwins’ of polytypes mentioned above. Interesting examples are the oriented intergrowths of the TiO_2 polymorphs rutile, anatase and brookite. In this respect, the high-resolution transmission electron microscopy (HRTEM) studies of hydrothermally coarsened TiO_2 nanoparticles by Penn & Banfield (1998), showing the structures of anatase $\{121\}$ reflection twin boundaries and of $\{112\}$ anatase– (100) brookite interfaces on an atomic scale, are noteworthy.

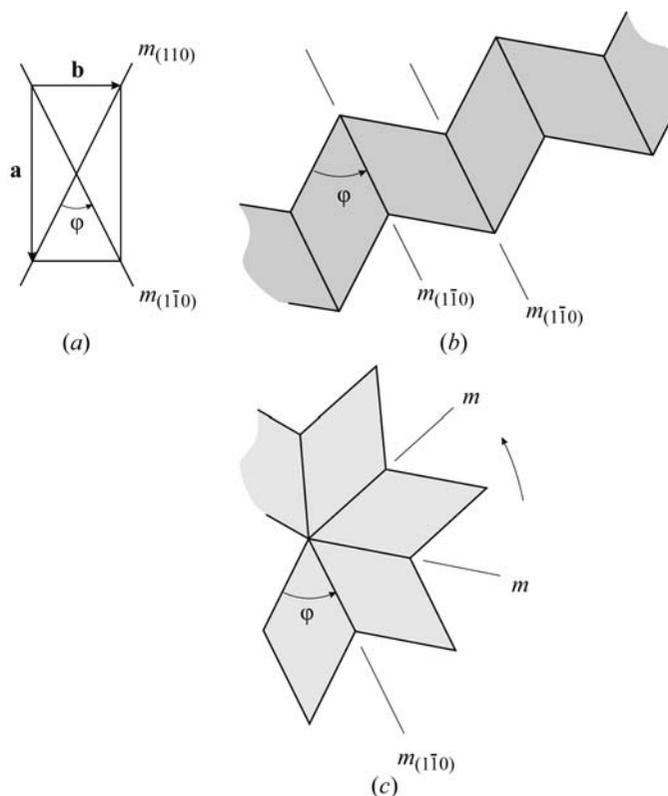


Fig. 3.3.3.1. Schematic illustration of simple (polysynthetic) and multiple (cyclic) twins. (a) Equivalent twin mirror planes (110) and $(1\bar{1}0)$ of an orthorhombic crystal. (b) Simple (polysynthetic) twin with two orientation states due to parallel repetition of the same twin mirror plane $(1\bar{1}0)$; the twin components are represented by $\{110\}$ rhombs. (c) Multiple (cyclic) twin with several (more than two) orientation states due to cyclic repetition of equivalent twin mirror planes of type $\{110\}$.

(iii) *Plesiotwins* (Nespolo, Ferraris *et al.*, 1999): oriented crystal associations based on a large coincidence-site lattice (CSL). The composition plane has a low degree of restoration of lattice nodes and the relative rotations between individuals are noncrystallographic. In the phlogopite from Mutsure-jima, Japan, both ordinary twins and plesiotwins are reported (Sunagawa & Tomura, 1976).

3.3.3. Morphological classification, simple and multiple twinning

Before discussing the symmetry features of twinning in detail, it is useful to introduce the terms ‘simple’ and ‘multiple’ twins, which are sometimes grouped under the heading ‘repetitive or repeated twins’. This is followed by some morphological aspects of twinning.

Simple twins are aggregates that consist of domains of only *two* orientation states, irrespective of the number, size and shape of the individual domains, Fig. 3.3.3.1(b). Thus, only *one* orientation relation (one twin law) exists. Contact twins and polysynthetic twins (see Section 3.3.3.1 below) are simple twins, as are the spinel penetration twins.

Multiple twins are aggregates that contain domains of *three* or more orientation states, *i.e.* at least *two* twin laws are involved. Two cases have to be distinguished:

(i) The twin elements are *symmetry-equivalent* with respect to the *eigensymmetry* group \mathcal{H} of the crystal (cf. Section 3.3.4.1). A typical example is provided by the equivalent (110) and $(1\bar{1}0)$ twin mirror planes of an orthorhombic crystal (*e.g.* aragonite), which frequently lead to *cyclic twins* (cf. Figs. 3.3.3.1a and c).

(ii) The twin elements are *not equivalent* with respect to the *eigensymmetry* of the crystal, *i.e.* several independent twin laws occur simultaneously in the twinned crystal. A typical example is

3.3. TWINNING OF CRYSTALS

provided by a Brazil twin of quartz, with each Brazil domain containing Dauphiné twins. This results in four domain states and three twin laws; *cf.* Example 3.3.6.4.

The distinction of simple and multiple twins is important for the following morphological classification. Further examples are given in Section 3.3.6.

3.3.3.1. Morphological classification

The morphology of twinned crystals, even for the same species and the same orientation relation, can be quite variable. For a given orientation relation the morphology depends on the geometry of the twin boundary as well as on the number of twin partners. A typical morphological feature of growth-twinned crystals is the occurrence of re-entrant angles. These angles are responsible for an increased growth velocity parallel to the twin boundary. This is the reason why twinned crystals often grow as platelets parallel to the composition plane (*cf.* Section 3.3.7.1). Detailed studies of the morphology of twins *versus* untwinned crystals were carried out as early as 1911 by Becke (1911). As a general observation, twinned crystals grow larger than untwinned crystals in the same batch.

The following classification of twins is in use:

(i) *Contact twins*. Two twin partners are in contact across a single composition plane $\pm(hkl)$, the Miller indices h, k, l of which have the same values for both partners ('common' plane). The contact plane usually has low indices. For reflection twins, the composition plane is frequently parallel to the twin mirror plane [see, however, Note (4) in Section 3.3.2.4]. Examples are shown in Fig. 3.3.6.3 for gypsum, in Fig. 3.3.6.7 for calcite and in Fig. 3.3.6.8(a) for a spinel (111) twin. In most cases, contact twins are growth twins.

(ii) *Polysynthetic (lamellar) twins* are formed by repetition of contact twins and consist of a linear sequence of domains with two alternating orientation states (Fig. 3.3.3.1b). The contact planes are parallel (lamellar twinning). This is typical for reflection twins if the twin mirror plane and the composition plane coincide. An illustrative example is the albite growth twin shown in Fig. 3.3.6.13. Polysynthetic twins may occur in growth, transformation and deformation twinning.

(iii) *Penetration twins*. The name 'penetration twin' results from the apparent penetration of two or more (idiomorphic) single crystals. The most prominent examples are twins of the spinel law in cubic crystals (*e.g.* spinels, fluorite, diamond). The spinel law is a reflection across (111) or a twofold rotation around [111]. Ideally these twins appear as two interpenetrating cubes with a common threefold axis, each cube representing one domain state, Fig. 3.3.6.8(b). In reality, these twins usually consist of 12 pyramid-shaped domains, six of each domain state, all originating from a common point in the centre of the twinned crystal (as shown in Figs. 3.3.6.6 and 3.3.6.8). Another famous example is the Carlsbad twin of orthoclase feldspar with [001] as a twofold twin axis (Fig. 3.3.7.1). Penetration twins are always growth twins.

(iv) *Cyclic twins and sector twins*. In contrast to the linear sequence of domains in polysynthetic twins, *cyclic twins* form a circular arrangement of domains of suitable shape. They are always multiple twins (three or more orientations states) which are (formally) generated by successive application of equivalent twin laws. The twin aggregate may form a full circle or a fraction of a circle (see Figs. 3.3.3.1c, 3.3.6.9 and 3.3.6.12). Impressive examples are the 'sixlings' and 'eightlings' of rutile (Fig. 3.3.6.11, *cf.* Example 3.3.6.10).

A special case of cyclic twins is provided by *sector twins*. Three or more domains of nearly triangular shape (angular sectors) extend from a common centre to form a twinned crystal with a more or less regular polygonal outline. The boundaries between two sector domains are usually planar and low-indexed. Such twins can be interpreted in two ways:

(a) they can be described by repeated action of (equivalent) reflection planes or twofold twin axes with suitable angular spacings;

(b) they can be described by approximate twin rotation axes of order three or more (including noncrystallographic axes such as fivefold); *cf.* Section 3.3.2.3.2 and Note (6) in Section 3.3.2.4.

Prominent examples are the growth twins of NH_4LiSO_4 (Fig. 3.3.7.2), aragonite (Fig. 3.3.2.4), K_2SO_4 (Fig. 3.3.6.9) and certain alloys with pseudo-fivefold twin axes (Fig. 3.3.6.10). Cyclic and sector twins are always growth twins.

(v) *Mimetic twins*. The term 'mimetic' is often applied to growth twins which, by their morphology, simulate a higher crystal symmetry. Regular penetration twins and sector twins are frequently also 'mimetic' twins. Particularly impressive examples are the harmotome and phillipsite twins, where monoclinic crystals, by multiple twinning, simulate higher symmetries up to a cubic rhomb-dodecahedron, described in Section 3.3.6.16(iii).

(vi) Common names of twins. In addition to the morphological description of twins mentioned above, some further shape-related names are in use:

(a) dovetail twins (prominent example: gypsum, *cf.* Figs. 3.3.4.1 and 3.3.6.3);

(b) elbow twins (rutile, cassiterite, *cf.* Fig. 3.3.6.11a);

(c) arrowhead twins (diamond);

(d) iron-cross twins (pyrite);

(e) butterfly twins (perovskite).

It is obvious from the morphological features of twins, described in this section, that crystals – by means of twinning – strive to simulate higher symmetries than they actually have. This will be even more apparent in the following section, which deals with the composite symmetry of twins and the twin law.

3.3.4. Composite symmetry and the twin law

In this section we turn our attention to the symmetry relations in twinning. The starting point of all symmetry considerations is the *eigensymmetry* \mathcal{H} of the untwinned crystal, *i.e.* the point group or space group of the single crystal, irrespective of its orientation and location in space. All domain states of a twinned crystal have the same (or the enantiomorphic) *eigensymmetry* but may exhibit different orientations. The orientation states of each two twin components are related by a twin operation k which cannot be part of the *eigensymmetry* \mathcal{H} . The term *eigensymmetry* is introduced here in order to provide a short and crisp distinction between the symmetry of the untwinned crystal (single-domain state) and the composite symmetry \mathcal{K} of a twinned crystal, as defined below. It should be noted that in crystal morphology the term *eigensymmetry* is also used, but with another meaning, in connection with the symmetry of face forms of crystals (Hahn & Klapper, 2005, pp. 764 and 791).

3.3.4.1. Composite symmetry

For a comprehensive characterization of the symmetry of a twinned crystal, we introduce the important concept of *composite symmetry* \mathcal{K} . This symmetry is defined as the extension of the *eigensymmetry* group \mathcal{H} by a twin operation k . This extension involves, by means of left (or right) *coset composition* $k \times \mathcal{H}$, the generation of further twin operations until a supergroup is obtained. This supergroup is the composite symmetry group \mathcal{K} .

In the language of group theory, the relation between the composite symmetry group \mathcal{K} and the *eigensymmetry* group \mathcal{H} can be expressed by a (left) coset decomposition of the supergroup \mathcal{K} with respect to the subgroup \mathcal{H} :

$$\mathcal{K} = k_1 \times \mathcal{H} \cup k_2 \times \mathcal{H} \cup k_3 \times \mathcal{H} \cup \dots \cup k_i \times \mathcal{H},$$

where k_1 is the identity operation; $k_1 \times \mathcal{H} = \mathcal{H} \times k_1 = \mathcal{H}$.

The number i of cosets, including the subgroup \mathcal{H} , is the *index* $[i]$ of \mathcal{H} in \mathcal{K} ; this index corresponds to the number of different