

## 3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

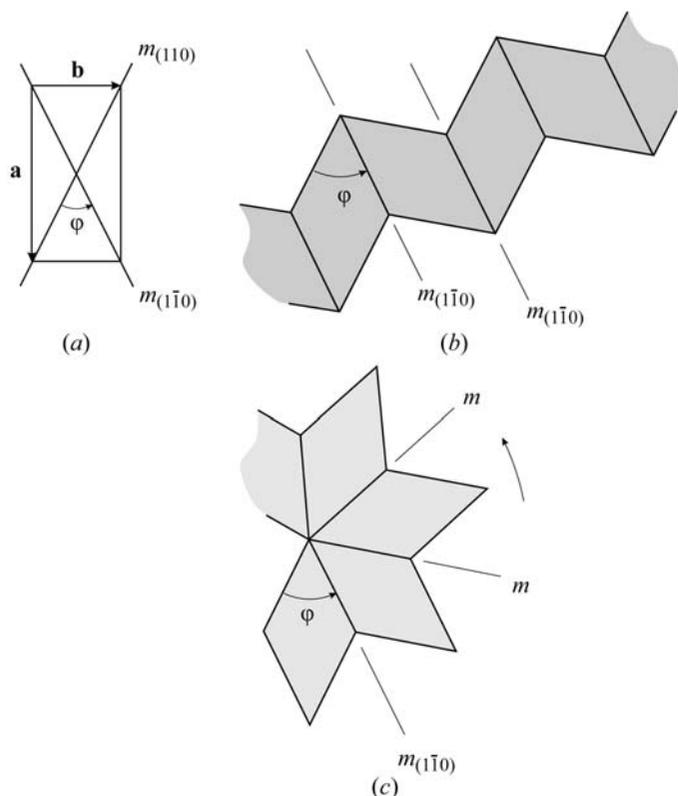


Fig. 3.3.3.1. Schematic illustration of simple (polysynthetic) and multiple (cyclic) twins. (a) Equivalent twin mirror planes (110) and  $(1\bar{1}0)$  of an orthorhombic crystal. (b) Simple (polysynthetic) twin with two orientation states due to parallel repetition of the same twin mirror plane  $(1\bar{1}0)$ ; 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}.

and brookite. In this respect, the high-resolution transmission electron microscopy (HRTEM) studies of hydrothermally coarsened  $\text{TiO}_2$  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.

(iii) *Plesiotwins* (Nespolo, Kogure & Ferraris, 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 below) are simple 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 symmetrically *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 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 3.3.6.3.

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. 3.3.6.1 for gypsum, in Fig. 3.3.6.5 for calcite and in Fig. 3.3.6.6(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. 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. 3.3.6.11. 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. 3.3.6.6b). 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. 3.3.6.4 and 3.3.6.6). 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, 3.3.6.7 and 3.3.6.10). Impressive examples are the ‘sixlings’ and ‘eightlings’ of rutile (Fig. 3.3.6.9, *cf.* Example 3.3.6.9).

### 3.3. TWINNING OF CRYSTALS

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 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  $\text{NH}_4\text{LiSO}_4$  (Fig. 3.3.7.2), aragonite (Fig. 3.3.2.4),  $\text{K}_2\text{SO}_4$  (Fig. 3.3.6.7) and certain alloys with pseudo-fivefold twin axes (Fig. 3.3.6.8). 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.

(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. Fig. 3.3.4.1);

(b) elbow twins (rutile, cassiterite, cf. Fig. 3.3.6.9a);

(c) arrowhead twin (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 morphology the term *eigensymmetry* is also used, but with another meaning, in connection with the symmetry of face forms of crystals (Hahn & Klapper, 2002).

##### 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  $\mathcal{H}$ :

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

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 orientation states in the twinned crystal. If  $\mathcal{H}$  is a normal subgroup of  $\mathcal{K}$ , which is always the case if  $i=2$ , then  $k \times \mathcal{H} = \mathcal{H} \times k$ , i.e. left and right coset decomposition leads to the same coset. The relation that the number of different orientation states  $n$  equals the index  $[i]$  of  $\mathcal{H}$  in  $\mathcal{K}$ , i.e.  $n = [i] = |\mathcal{K}| : |\mathcal{H}|$ , was first expressed by Zheludev & Shuvalov (1956, p. 540) for ferroelectric phase transitions.

These group-theoretical considerations can be translated into the language of twinning as follows: although the *eigensymmetry*  $\mathcal{H}$  and the composite symmetry  $\mathcal{K}$  can be treated either as point groups (finite order) or space groups (infinite order), in this and the subsequent sections twinning is considered only in terms of point groups [see, however, Note (8) in Section 3.3.2.4, as well as Section 3.3.10.4]. With this restriction, the number of twin operations in each coset equals the order  $|\mathcal{H}|$  of the *eigensymmetry* point group  $\mathcal{H}$ . All twin operations in a coset represent the same orientation relation, i.e. each one of them transforms orientation state 1 into orientation state 2. Thus, the complete coset characterizes the orientation relation comprehensively and is, therefore, defined here as the *twin law*. The different operations in a coset are called *alternative twin operations*. A further formulation of the twin law in terms of black–white symmetry will be presented in Section 3.3.5. Many examples are given in Section 3.3.6.

This extension of the ‘classical’ definition of a twin law from a single twin operation to a complete coset of alternative twin operations does not conflict with the traditional description of a twin by the one morphologically most prominent twin operation. In many cases, the morphology of the twin, e.g. re-entrant angles or the preferred orientation of a composition plane, suggests a particular choice for the ‘representative’ among the alternative

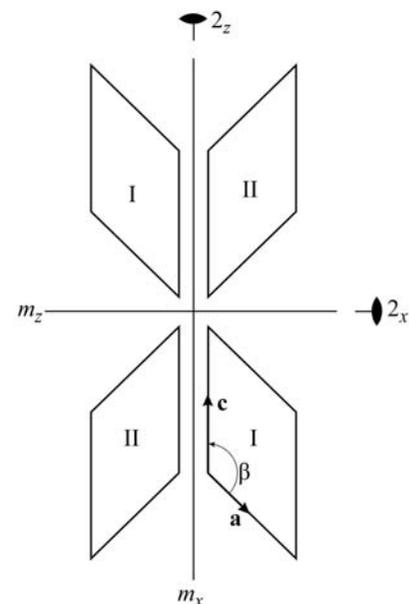


Fig. 3.3.4.1. Gypsum dovetail twin: schematic illustration of the coset of alternative twin operations. The two domain states I and II are represented by oriented parallelograms of *eigensymmetry*  $2_y/m_y$ . The subscripts  $x$  and  $z$  of the twin operations refer to the coordinate system of the orthorhombic composite symmetry  $\mathcal{K}_D$  of this twin;  $a$  and  $c$  are the monoclinic coordinate axes.