

## 3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

states. The group-theoretical treatment of this process, based on the *full eigensymmetry*, results in the infinite composite symmetry group  $\mathcal{K} = \infty/m\bar{m}$ , with the rotation axis parallel to the twofold axis of the intersection symmetry  $112/m$ , common to all these infinitely many domains. In an even more general case, for example an orthorhombic crystal with twin reflection plane  $(111)$ , the infinite sphere group  $\mathcal{K} = m\bar{3}2$  would result as composite symmetry. Neither of these cases is physically meaningful and thus they are not considered further here. It is emphasized, however, that the *reduced* composite symmetry  $\mathcal{K}^*$  for any pair of domains in contact, as derived in case (II) above, is finite and crystallographic and, thus, of practical use.

(iii) *Pseudo-crystallographic composite symmetry*. Among twins with noncrystallographic composite symmetry, described above, those exhibiting structural or at least metrical pseudo-symmetries are of special significance. Again we consider an orthorhombic crystal with *eigensymmetry*  $\mathcal{H} = 2/m2/m2/m$  and equivalent twin reflection planes  $(110)$  and  $(\bar{1}\bar{1}0)$ , but now with a special axial ratio  $b/a \approx |\tan(360^\circ/n)|$  ( $n = 3, 4$  or  $6$ ).

The procedure described above in (ii) leads to three different orientation states for  $n = 3$  and  $6$  and to two different orientation states for  $n = 4$ , forming a cyclic arrangement of sector domains (for cyclic and sector twins see Section 3.3.3). The intersection group  $\mathcal{H}^*$  of all these domain states is  $112/m$ , with the twofold axis along the  $c$  axis. The reduced composite symmetry of any pair of domains in contact is orthorhombic of type  $\mathcal{K}^* = 2'/m'2'/m'2/m$ .

These multiple cyclic twins can be described in two ways (*cf.* Section 3.3.2.3.2):

(a) by repeated application of equivalent binary twin operations (reflections or twofold rotations) to a pseudosymmetrical crystal, as proposed by Hartman (1960) and Curien (1960). Note that each one of these binary twin operations is 'exact', whereas the closure of the cycle of sectors is only approximate; the deviation from  $360^\circ/n$  depends on the (metrical) pseudosymmetry of the lattice;

(b) by successive application of pseudo  $n$ -fold twin rotations around the zone axis of the equivalent twin reflection planes. Note that the individual rotation angles are not exactly  $360^\circ/n$ , due to the pseudosymmetry of the lattice. This alternative description corresponds to the approach by Friedel (1926, p. 435) and Buerger (1960b).

It is now reasonable to define an *extended composite symmetry*  $\mathcal{K}(n)$  by adding the  $n$ -fold rotation as a further generator to the reduced composite symmetry  $\mathcal{K}^*$  of a domain pair. This results in the composite symmetry  $\mathcal{K}(n)$  of the complete twin aggregate, in the present case in a modification of the symmetry  $\mathcal{K}^* = 2'/m'2'/m'2/m$  to:

$\mathcal{K}(6) = \mathcal{K}(3) = 6(2)/m2/m2/m$  (three orientation states, two twin laws) for  $n = 3$  and  $n = 6$ ;

$\mathcal{K}(4) = 4(2)/m2/m2/m$  (two orientation states, one twin law) for  $n = 4$ .

The *eigensymmetry* component of the main twin axis is given in parentheses.

This construction can also be applied to noncrystallographic twin rotations  $n = 5, 7, 8$  etc. (*cf.* Section 3.3.6.8):

$\mathcal{K}(10) = \mathcal{K}(5) = 10(2)/m2/m2/m$  (five orientation states, four twin laws) for  $n = 5$  and  $n = 10$ .

The above examples are based on a twofold *eigensymmetry* component along the  $n$ -fold twin axis. An example of a pseudo-hexagonal twin, monoclinic gibbsite,  $\text{Al}(\text{OH})_3$ , without a twofold *eigensymmetry* component along  $[001]$ , is treated as Example 3.3.6.10 and Fig. 3.3.6.10.

It is emphasized that the considerations of this section apply not only to the particularly complicated cases of multiple growth twins but also to transformation twins resulting from the loss of higher-order rotation axes that is accompanied by a small metrical deformation of the lattice. As a result, the extended

composite symmetries  $\mathcal{K}(n)$  of the transformation twins resemble the symmetry  $\mathcal{G}$  of their parent phase. The occurrence of both multiple growth and multiple transformation twins of orthorhombic pseudo-hexagonal  $\text{K}_2\text{SO}_4$  is described in Example 3.3.6.7.

*Remark.* It is possible to construct multiple twins that cannot be treated as a cyclic sequence of binary twin elements. This case occurs if a pair of domain states 1 and 2 are related only by an  $n$ -fold rotation or roto-inversion ( $n \geq 3$ ). The resulting coset again contains the alternative twin operations, but in this case *only* for the orientation relation  $1 \Rightarrow 2$ , and not for  $2 \Rightarrow 1$  ('non-transposable' domain pair). This coset procedure thus does not result in a composite group for a domain pair. In order to obtain the composite group, further cosets have to be constructed by means of the higher powers of the twin rotation under consideration. Each new power corresponds to a further domain state and twin law.

This construction leads to a composite symmetry  $\mathcal{K}(n)$  of supergroup index  $[i] \geq 3$  with respect to the *eigensymmetry*  $\mathcal{H}$ . This case can occur only for the following  $\mathcal{H} \Rightarrow \mathcal{K}$  pairs:  $1 \Rightarrow 3, \bar{1} \Rightarrow \bar{3}, 1 \Rightarrow 4, \bar{1} \Rightarrow \bar{4}, m \Rightarrow 4/m, 1 \Rightarrow 6, m \Rightarrow \bar{6} = 3/m, m \Rightarrow 6/m, 2/m \Rightarrow 6/m$  (monoaxial point groups), as well as for the two cubic pairs  $222 \Rightarrow 23, mmm \Rightarrow 2/m\bar{3}$ . For the pairs  $1 \Rightarrow 3, \bar{1} \Rightarrow \bar{3}, m \Rightarrow \bar{6} = 3/m, 2/m \Rightarrow 6/m$  and the two cubic pairs  $222 \Rightarrow 23, mmm \Rightarrow 2/m\bar{3}$ , the  $\mathcal{K}$  relations are of index [3] and imply three non-transposable domain states. For the pairs  $1 \Rightarrow 4, \bar{1} \Rightarrow \bar{4}, m \Rightarrow 4/m$ , as well as  $1 \Rightarrow 6$  and  $m \Rightarrow 6/m$ , four or six different domain states occur. Among them, however, domain pairs related by the second powers of 4 and 4 as well as by the third powers of 6 and 6 operations are transposable, because these twin operations correspond to twofold rotations.

No growth twins of this type are known so far. As transformation twin, langbeinite ( $23 \Leftrightarrow 222$ ) is the only known example.

## 3.3.5. Description of the twin law by black–white symmetry

An alternative description of twinning employs the symbolism of colour symmetry. This method was introduced by Curien & Le Corre (1958) and by Curien & Donnay (1959). In this approach, a colour is attributed to each different domain state. Depending on the number of domain states, simple twins with two colours (*i.e.* 'black–white' or 'dichromatic' or 'anti-symmetry' groups) and multiple twins with more than two colours (*i.e.* 'polychromatic' symmetry groups) have to be considered. Two kinds of operations are distinguished:

(i) The symmetry operations of the *eigensymmetry* (point group) of the crystal. These operations are 'colour-preserving' and form the 'monochromatic' *eigensymmetry* group  $\mathcal{H}$ . The symbols of these operations are unprimed.

(ii) The twin operations, *i.e.* those operations which transform one orientation state into another, are 'colour-changing' operations. Their symbols are designated by a prime if of order 2:  $2', m', \bar{1}'$ .

For *simple twins*, all colour-changing (twin) operations are binary, hence the two domain states are transposable. The composite symmetry  $\mathcal{K}$  of these twins thus can be described by a 'black-and-white' symmetry group. The coset, which defines the twin law, contains only colour-changing (primed) operations. This notation has been used already in previous sections.

It should be noted that symbols such as  $4'$  and  $6'$ , despite appearance to the contrary, represent *binary* black-and-white operations, because  $4'$  contains 2, and  $6'$  contains 3 and  $2'$ , with  $2'$  being the twin operation. For this reason, these symbols are written here as  $4'(2)$  and  $6'(3)$ , whereby the unprimed symbol in parentheses refers to the *eigensymmetry* part of the twin axis. In

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contrast,  $6'(2)$  would designate a (polychromatic) twin axis which relates three domain states (three colours), each of *eigensymmetry* 2. Twin centres of symmetry  $\bar{1}'$  are always added to the symbol in order to bring out an inversion twinning contained in the twin law. In the original version of Curien & Donnay (1959), the black–white symbols were only used for twinning by merohedry. In the present chapter, the symbols are also applied to non-merohedral twins, as is customary for (ferroelastic) domain structures. This has the consequence, however, that the *eigensymmetries*  $\mathcal{H}$  or  $\mathcal{H}'$  and the composite symmetries  $\mathcal{K}$  or  $\mathcal{K}'$  may belong to different crystal systems and, thus, are referred to different coordinate systems, as shown for the composite symmetry of gypsum in Section 3.3.4.1.

For the treatment of *multiple twins*, ‘polychromatic’ composite groups  $\mathcal{K}(n)$  are required. These contain colour-changing operations of order higher than 2, *i.e.* they relate three or more colours (domain states). Consequently, not all pairs of domain states are transposable. This treatment of multiple twins is rather complicated and only sensible if the composite symmetry group is finite and contains twin axes of low order ( $n \leq 8$ ). For this reason, the symbols for the composite symmetry  $\mathcal{K}$  of multiple twins are written without primes; see the examples in Section 3.3.4.4(iii).

#### 3.3.6. Examples of twinned crystals

In order to illustrate the foregoing rather abstract deliberations, an extensive set of examples of twins occurring either in nature or in the laboratory is presented below. In each case, the twin law is described in two ways: by the coset of alternative twin operations and by the black–white symmetry symbol of the composite symmetry  $\mathcal{K}$ , as described in Sections 3.3.4 and 3.3.5.

For the description of a twin, the conventional crystallographic coordinate system of the crystal and its *eigensymmetry* group  $\mathcal{H}$  are used in general; exceptions are specifically stated. To indicate the orientation of the twin elements (both rational and irrational) and the composition planes, no specific convention has been adopted; rather a variety of intuitively understandable simple symbols are chosen for each particular case, with the additional remark ‘rational’ or ‘irrational’ where necessary. Thus, for twin reflection planes and (planar) twin boundaries symbols such as  $m_x$ ,  $m(100)$ ,  $m \parallel (100)$  or  $m \perp [100]$  are used, whereas twin rotation axes are designated by  $2_z$ ,  $2_{[001]}$ ,  $2 \parallel [001]$ ,  $2 \perp (001)$ ,  $3_z$ ,  $3_{[111]}$ ,  $4_{[001]}$  *etc.*

##### 3.3.6.1. Inversion twins in orthorhombic crystals

The (polar)  $180^\circ$  twin domains in a (potentially ferroelectric) crystal of *eigensymmetry*  $\mathcal{H} = mm2$  ( $m_x m_y 2_z$ ) and composite symmetry  $\mathcal{K} = 2/m 2/m 2/m$  (*e.g.* in  $\text{KTiOPO}_4$ ,  $\text{NH}_4\text{LiSO}_4$ , Li-formate monohydrate) result from a group–subgroup relation of index  $[i] = 2$  with invariance of the symmetry framework (merohedral twins), but antiparallel orientation of the polar axes. The orientation relation between the two domain states is described by the coset  $k \times \mathcal{H}$  of twin operations shown in Table 3.3.6.1, whereby the reflection in (001),  $m_z$ , is considered as the ‘representative’ twin operation.

Table 3.3.6.1. Orthorhombic inversion twins: coset of alternative twin operations (twin law)

$\mathcal{H}$	$k \times \mathcal{H} = m_z \times \mathcal{H}$
1	$m_z$ (normal to the polar axis [001])
$m_x$	$2_x$ (normal to the polar axis)
$m_y$	$2_y$ (normal to the polar axis)
$2_z$	$\bar{1}$ (inversion)

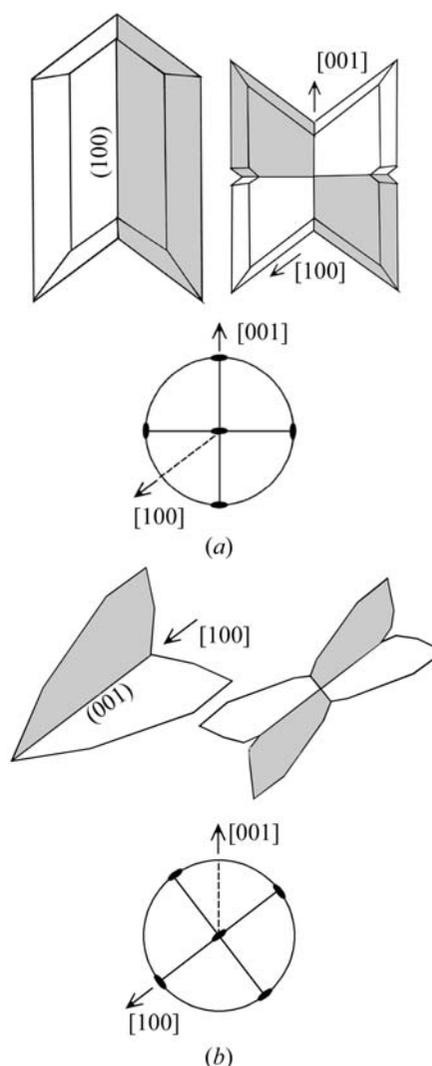


Fig. 3.3.6.1. Dovetail twin (a) and Montmartre twin (b) of gypsum. The two orientation states of each twin are distinguished by shading. For each twin type (a) and (b), the following aspects are given: (i) two idealized illustrations of each twin, on the left in the most frequent form with two twin components, on the right in the rare form with four twin components, the morphology of which displays the orthorhombic composite symmetry; (ii) the oriented composite symmetry in stereographic projection (dotted lines indicate monoclinic axes).

Hence, these twins can be regarded not only as reflection, but also as rotation or inversion twins. The composite symmetry, in black–white symmetry notation, is

$$\mathcal{K} = \frac{2'_x 2'_y 2'_z}{m_x m_y m'_z} (\bar{1}'),$$

whereby the primed symbols designate the (alternative) twin operations (*cf.* Section 3.3.5).

##### 3.3.6.2. Twinning of gypsum

The *dovetail twin* of gypsum [*eigensymmetry*  $\mathcal{H} = 1 2/m 1$ , with twin reflection plane  $m \parallel (100)$ ], coset of twin operations  $k \times \mathcal{H}$  and composite symmetry  $\mathcal{K}$ , was treated in Section 3.3.4. Gypsum exhibits an independent additional kind of growth twinning, the *Montmartre twin* with twin reflection plane  $m \parallel (001)$ . These two twin laws are depicted in Fig. 3.3.6.1. The two cosets of twin operations in Table 3.3.6.2 and the symbols of the composite symmetries  $\mathcal{K}_D$  and  $\mathcal{K}_M$  of both twins are referred, in addition to the monoclinic crystal axes, also to orthorhombic axes  $x_D, y, z_D$  for dovetail twins and  $x_M, y, z_M$  for Montmartre twins. This procedure brings out for each case the perpendicularity of the