

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

sulfate, which can only be grown from aqueous solution and which frequently develops pseudo-hexagonal growth twins with three orientation states. Above about 353 K, the grown-in domains can easily be switched stepwise from one domain state into another by an appropriate shear stress, without the sample ever undergoing a phase transition. Ammonium sulfate exhibits a virtual phase transition into a hexagonal prototype phase. It decomposes, however, at about 473 K, well before reaching the phase transition.

There are many examples (e.g. Rochelle salt) in which a ferroelastic domain structure can be generated by a real phase transition as well as by growth below the transition temperature. As a rule, the domain textures of growth and transformation twins are quite different. A detailed account of ferroelastic crystals is given by Salje (1993); a review is provided by Abrahams (1994).

(iii) *Ferrobielastic twinning*. Ferroelastic twinning implies a switchable spontaneous strain, i.e. a change of the unit-cell orientation in the different domains (*twinning with change of form*; Klassen-Neklyudova, 1964). In some species of crystals, however, mechanical twinning *without* change of the unit-cell orientation is possible (*twinning without change of form*). This can occur, for example, in trigonal crystals with a hexagonal *P* lattice. Here, the shape and orientation of the unit cell does not change from one domain to the other, and the twin is always merohedral (cf. Section 3.3.9). The atomic structure within the unit cell, however, is altered by the switching. The most famous example is the Dauphiné twinning of quartz, which can be induced by uniaxial stress along an appropriate direction. This effect was observed a long time ago by Judd (1888) and described in detail by Schubnikow & Zinserling (1932) and Zinserling & Schubnikow (1933). The ‘critical stress’ for the Dauphiné switching decreases with increasing temperature and becomes zero at the transition to the hexagonal phase at 846 K.

The property of a crystal to form ‘twins without change of form’ under mechanical stress was called *ferrobielasticity* by Newnham (1975). Aizu (1973) speaks of *second-order (ferroelastic) state shifts*. It implies a change in the orientation of some tensorial properties. For Dauphiné twins of quartz, it is the elastic (fourth-rank) tensor that is responsible for the switching of the structure. Under uniaxial stress, a direction of high Young’s modulus⁴ is transformed into a (compatible) direction of smaller Young’s modulus for which the material responds with a higher elastic yield. Note that this switching is induced by both compressive *and* tensile stress. A derivation of all crystal species capable of *second-order ferroic state shifts* by electric fields and mechanical stress, including a series of photographs showing the development of Dauphiné twins of quartz under stress, is presented by Aizu (1973).

For trigonal crystals with a *rhombohedral (R)* lattice, on the other hand, this switching implies the change of the obverse into the reverse rhombohedron and *vice versa*. In this case, the orientation of the primitive rhombohedral unit cell is changed, leading to ‘twinning with change of form’ (i.e. not to ferrobielasticity), even though the orientation of the triple hexagonal cell is not changed. This kind of twinning corresponds to the (0001) reflection twins of rhombohedral crystals and the (111) spinel twins of cubic crystals (cf. Examples 3.3.6.6 and 3.3.6.7). The switching from a cubic obverse rhombohedron into the reverse one actually takes place in the ‘ $\Sigma 3$ deformation twins’ of cubic metals [cf. part (i) above].

(iv) *Detwinning*. The generation of twins by mechanical stress allows, in reverse, the *detwinning* of crystals by the application of appropriate stress. This method has been extensively used for the elimination of Dauphiné twins in quartz (Thomas & Wooster, 1951; Klassen-Neklyudova, 1964, pp. 75–86). The presence of

these ‘electrical’ twins impairs the function of piezoelectric devices, such as piezoelectric resonators, made from these crystals (Iliescu & Chirila, 1995; Iliescu *et al.*, 1997). Brazil twins of quartz, which also entail the reversal of the electric axes (cf. Fig. 3.3.6.4) cannot be detwinned. Mechanical detwinning by appropriate stress is also used to obtain single-domain crystals of the ferroelastic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ high- T_c superconductor. In most cases, elevated temperatures reduce the critical stress required for domain switching.

It is characteristic of *ferroelectric* crystals that they can be switched into a single-domain state (i.e. ‘detwinned’ or ‘poled’) by a sufficiently strong (coercive) electric field of proper direction. It is, however, also possible to detwin *ferroelastic domains* by the application of electric fields. This occurs in *ferroelectric–ferroelastic* crystals, where ferroelectricity and ferroelasticity are coupled, i.e. where the reversal of the electric polarity is accompanied by (mechanical) switching of the ferroelastic domains into the other deformation state and *vice versa*. An outstanding and well known example is Rochelle salt, which undergoes an orthorhombic–monoclinic phase transition $222 \longleftrightarrow 2$ at about 297 K with coupled ferroelectricity and ferroelasticity in the monoclinic phase (cf. Zheludev, 1971, pp. 143, 226). An extensive crystal-optical study of the ferroelastic domain switching and detwinning in Rochelle salt by electric fields, including film records of the domain movements, was presented by Chernysheva [1951, 1955; quoted after Klassen-Neklyudova (1964), pp. 75–78 and Fig. 100].

(v) *Non-ferroelastic and co-elastic twins*. Phase transitions with symmetry changes within the same crystal family also exhibit a spontaneous deformation of the unit cell, but all orientation states have the same deformation, both in magnitude and orientation. Hence, a domain switching is not possible (except for ferrobielastic crystals treated above). Therefore, this kind of phase transition and its associated domain structure are called *non-ferroelastic*. Salje (1993) uses the term *co-elastic*. In crystallography, twins resulting from this kind of phase transition are grouped under *twins by merohedry* (cf. Section 3.3.9). Typical examples of non-ferroelastic and co-elastic materials are quartz (merohedral Dauphiné twins, phase transition $P3_121 \longleftrightarrow P6_422$ at 846 K) and calcite (transition $R3c \longleftrightarrow R3m$ at about 1523 K, cf. Salje, 1993, Chapter 2).

In conclusion, it is pointed out that twins with one and the same twin law can be generated in different ways. In addition to the twins of potassium sulfate mentioned above [growth twins, transformation twins and mechanical (ferroelastic) twins], the Dauphiné twinning of quartz is an example: it can be formed during crystal growth, by a phase transition and by mechanical stress [ferrobielasticity, cf. part (iii) above]. As a rule, the domain textures of a twinned crystal are quite different for growth twins, transformation twins and mechanical twins.

3.3.8. Lattice aspects of twinning

In the previous sections of this chapter, the symmetry relations and the morphological classification of twins have been presented on a macroscopic level, i.e. in terms of point groups. It would be ideal if this treatment could be extended to atomic dimensions, i.e. if twinning could be explained and even predicted in terms of space groups, crystal structures, interface structures and structural defects. This approach is presently only possible for a few specific crystals; for the majority of twins, however, only general rules are known and qualitative predictions can be made.

An early and very significant step towards this goal was the introduction of the lattice concept in the treatment of twinning (three-periodic twins). This was first done about a hundred years ago – based on the lattice analysis of Bravais – by Mallard (1879)

⁴ Defined in Section 1.3.3.1.

3.3. TWINNING OF CRYSTALS

Table 3.3.8.1. *Lattice planes (hkl) and lattice rows [uvw] that are mutually perpendicular (after Koch, 2004)*

| Lattice | Lattice plane (hkl) | Lattice row [uvw] | Perpendicularity condition and quantity $j' = hu + kv + lw$ |
|---|----------------------------------|----------------------------------|---|
| Triclinic | — | — | — |
| Monoclinic (unique axis <i>b</i>) | (010) | [010] | — |
| Monoclinic (unique axis <i>c</i>) | (001) | [001] | — |
| Orthorhombic | (100) (010) (001) | [100] [010] [001] | — — — |
| Hexagonal and rhombohedral (hexagonal axes) | (<i>hki</i> 0) (0001) | [<i>uv</i> 0] [001] | $u = 2h + k, v = h + 2k, j' = 2h^2 + 2k^2 + 2hk$ — |
| Rhombohedral (rhombohedral axes) | (<i>h, k, -h - k</i>) (111) | [<i>u, v, -u - v</i>] [111] | $u = h, v = k, j' = 2h^2 + 2k^2 + 2hk$ — |
| Tetragonal | (<i>hk</i> 0) (001) | [<i>uv</i> 0] [001] | $u = h, v = k, j' = h^2 + k^2$ — |
| Cubic | (<i>hkl</i>) | [<i>uvw</i>] | $u = h, v = k, w = l; j' = h^2 + k^2 + l^2$ |

and especially by Friedel (1904, 1926), in part before the advent of X-ray diffraction. The book by Friedel (1926), particularly Chapter 15, is the most frequently cited reference in this field. Later, Friedel (1933) sharpened his theories to include two further types of twins: ‘*macles monopériodiques*’ and ‘*macles dipériodiques*’, in addition to the previous ‘*macles tripériodiques*’, see Section 3.3.8.2 below. These concepts were further developed by Niggli (1919, 1920/1924/1941).⁵

The lattice aspects of twinning (*triperiodic twins*) are discussed in this section and in Section 3.3.9. An important concept in this field is the *coincidence-site sublattice* of the twin in direct space and its counterpart in reciprocal space. Extensive use of the notion of coincidence-site lattices (CSLs) is made in *bicrystallography* for the study of grain boundaries, as briefly explained in Section 3.2.2.

The coincidence-site lattice and further related lattices (O- and DSC-lattices) were introduced into the study of bicrystals by Bollmann (1970, 1982) and were theoretically thoroughly developed by Grimmer (1989*a,b*, 2003). Their applications to grain boundaries are contained in the works by Sutton & Balluffi (1995) and Gottstein & Shvindlerman (1999).

3.3.8.1. Basic concepts of Friedel’s lattice theory

The basis of Friedel’s (1904, 1926) lattice theory of twinning is the postulate that the coincidence-site sublattice common to the two twin partners (twin lattice) suffers no deviation (strict condition) or at most a slight deviation (approximate condition) in crossing the boundary between the two twin components (composition plane). This purely geometrical condition is often expressed as ‘three-dimensional lattice control’ (Santoro, 1974, p. 225), which is supposed to be favourable to the formation of twins.

In order to define the coincidence sublattice (twin lattice) of the two twin partners, it is assumed that their oriented point lattices are infinitely extended and interpenetrate each other. The lattice classification of twins is based on the degree of coincidence of these two lattices. The criterion applied is the dimension of the *coincidence-site subset* of the two interpenetrating lattices, which is defined as the set of all lattice points common to both lattices, provided that two initial points, one from each lattice, are brought to coincidence (common origin). This common origin has the immediate consequence that the concept of the twin displacement vector \mathbf{t} – as introduced in Note (8) of Section 3.3.2.4 – does not apply here. The existence of the coincidence subset of a twin results from the *crystallographic orientation relation* (Section 3.3.2.2), which is a prerequisite for twinning. This subset is one-,

two- or three-dimensional (monoperiodic, diperiodic or triperiodic twins).

If a coincidence relation exists between lattices in direct space, a complementary superposition relation occurs for their reciprocal lattices. This superposition can often, but not always, be detected in the diffraction patterns of twinned crystals; cf. Section 3.3.11 below.

3.3.8.2. Lattice coincidences, twin lattice, twin lattice index

Four types of (exact) *lattice coincidences* have to be distinguished in twinning:

(i) *No coincidence* of lattice points (except, of course, for the initial pair). This case corresponds to arbitrary intergrowth of two crystals or to a general bicrystal.

(ii) *One-dimensional coincidence*: Both lattices have only *one lattice row* in common. Of the seven binary twin operations listed in Section 3.3.2.3.1, the following three generate one-dimensional lattice coincidence:

(a) twofold rotation around a (rational) lattice row normal to an irrational plane [twin operation (iii)];

(b) reflection across an irrational plane normal to a (rational) lattice row (note that the coincidence would be three-dimensional if this plane were rational) [twin operation (iv)];

(c) twofold rotation around an irrational axis normal to a (rational) lattice row (complex twin, *Kantennormalengesetz*) [twin operations (v) and (vi)].

Lattices are always centrosymmetric; hence, for lattices, as well as for centrosymmetric crystals, the first two twin operations above belong to the same twin law. For noncentrosymmetric crystals, however, the two twin operations define different twin laws.

(iii) *Two-dimensional coincidence*: Both lattices have only *one lattice plane* in common. The following two (of the seven) twin operations lead to two-dimensional lattice coincidence:

(a) reflection across a (rational) lattice plane [twin operation (i)];

(b) twofold rotation around an irrational axis normal to a (rational) lattice plane (note that the coincidence would be three-dimensional if this axis were rational) [twin operation (ii)].

Again, for lattices and centrosymmetric crystals both twin operations belong to the same twin law.

(iv) *Three-dimensional coincidence*: Here the coincidence subset is a three-dimensional lattice, the *coincidence-site lattice* or *twin lattice*. It is the three-dimensional sublattice common to the (equally or differently) oriented lattices of the two twin partners. The degree of three-dimensional lattice coincidence is defined by the *coincidence-site lattice index*, *twin lattice index* or *sublattice index* [j], for short: *lattice index*. This index is often called Σ , especially in metallurgy. It is the volume ratio of the primitive cells of the twin lattice and of the (original) crystal lattice (*i.e.* $1/j$

⁵ Two recent publications describe in detail the ‘French school of twinning’, with many references to the original papers: Boulliard (2010, in French) and Hardouin-Duparc (2011, in English).

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

is the ‘degree of dilution’ of the twin lattice with respect to the crystal lattice):

$$[j] = \Sigma = V_{\text{twin}}/V_{\text{crystal}}$$

The lattice index is always an integer: $j = 1$ means *complete* coincidence (parallelism), $j > 1$ *partial* coincidence of the two lattices. The index $[j]$ can also be interpreted as elimination of the fraction $(j - 1)/j$ of the lattice points, or as index of the translation group of the twin lattice in the translation group of the crystal lattice. The coincidence lattice, thus, is the intersection of the oriented lattices of the two twin partners.

Twinning with $[j] = 1$ has been called by Friedel (1926, p. 427) *twinning by merohedry* (*‘maclés par méridrie’*) (for short: *merohedral twinning*), whereas twinning with $[j] > 1$ is called *twinning by lattice merohedry* or *twinning by reticular merohedry* (*‘maclés par méridrie réticulaire’*) (Friedel, 1926, p. 444). The terms for $[j] = 1$ are easily comprehensible and in common use. The terms for $[j] > 1$, however, are somewhat ambiguous (the term ‘merohedral’ refers to point groups, not lattices). In the present section, therefore, the terms *sublattice*, *coincidence lattice* or *twin lattice* of index $[j]$ are preferred. Merohedral twinning is treated in detail in Section 3.3.9.

Complete and exact three-dimensional lattice coincidence ($[j] = 1$) always exists for inversion twins (of noncentrosymmetric crystals) [twin operation (vii)]. For reflection twins, complete or partial coincidence occurs if a (rational) lattice row $[uvw]$ is (exactly) perpendicular to the (rational) twin reflection plane (hkl); similarly for rotation twins if a (rational) lattice plane (hkl) is (exactly) perpendicular to the (rational) twofold twin axis $[uvw]$.

The systematic perpendicularity relations (*i.e.* relations valid independent of the axial ratios) for lattice planes (hkl) and lattice rows $[uvw]$ in the various crystal systems are collected in Table 3.3.8.1. No perpendicularity occurs for triclinic lattices (except for metrical accidents). The perpendicularity cases for monoclinic and orthorhombic lattices are trivial. For tetragonal (tet), hexagonal (hex) and rhombohedral (rhomb) lattices, systematic perpendicularity of planes and rows occurs only for the $[001]_{\text{tet}}$ and the $[001]_{\text{hex}}$ (or $[111]_{\text{rhomb}}$) zones, *i.e.* for planes parallel and rows perpendicular to these directions, in addition to the trivial cases $[001] \perp (001)$ or $[111] \perp (111)$. In cubic lattices, every lattice plane (hkl) is perpendicular to a lattice row $[uvw]$ (with $h = u$, $k = v$, $l = w$). More general coincidence relations were derived by Grimmer (1989a,b, 2003).

The index $[j]$ of a coincidence or twin lattice can often be obtained by inspection; it can be calculated by using a formula for the auxiliary quantity j' as follows:

$$j' = hu + kv + lw \quad (\text{scalar product } \mathbf{r}_{hkl}^* \cdot \mathbf{t}_{uvw})$$

with sublattice index

$$\begin{aligned} [j] &= |j'| \text{ for } j' = 2n + 1 \\ &= |j'|/2 \text{ for } j' = 2n. \end{aligned}$$

Here, the indices of the plane (hkl) and of the perpendicular row $[uvw]$ are referred to a primitive lattice basis (primitive cell). For centred lattices, described by conventional bases, modifications are required; these and further examples are given by Koch (2004). Formulae and tables are presented by Friedel (1926, pp. 245–252) and by Donnay & Donnay (1972). The various equations for the quantity j' are also listed in the last column of Table 3.3.8.1.

Note that in the tetragonal system for any ($hk0$) reflection twin and any $[uv0]$ twofold rotation twin, the coincidence lattices are also tetragonal and have the same lattice parameter c . Further details are given by Grimmer (2003). An analogous relation applies to the hexagonal crystal family for ($hki0$) and $[uv0]$ twins. In the cubic system, the following types of twin lattices occur:

(111) and $[111]$ twins: hexagonal P lattice (*e.g.* spinel twins);
($hk0$) and $[uv0]$ twins: tetragonal lattice;
(hhl) and $[uvw]$ twins: orthorhombic lattice;
(hkl) and $[uvw]$ twins: monoclinic lattice.

Note that triclinic twin lattices are not possible for a cubic lattice.

After these general considerations of coincidence-site and twin lattices and their lattice index, specific cases of ‘triperiodic twins’ are treated in Section 3.3.8.3. In addition to the characterization of the twin lattice by its index $[j]$, the Σ notation used in metallurgy is included.

3.3.8.3. Twins with three-dimensional twin lattices (*‘triperiodic’ twins*)

The following cases of exact superposition are distinguished:

(i) *Twins with $[j] = 1$ ($\Sigma 1$ twins)*. Here, the crystal lattice and the twin lattice are identical, *i.e.* the coincidence (parallelism) of the two oriented crystal lattices is complete. Hence, any twin operation must be a symmetry operation of the point group of the lattice (holohedry), but not of the point group of the crystal. Consequently, this twinning can occur in ‘merohedral’ point groups only. This *twinning by merohedry (parallel-lattice twins, twins with parallel axes)* will be treated extensively in Sections 3.3.9 and 3.3.11.3; *cf.* Klapper & Hahn (2010).

(ii) *Twins with $[j] = 2$ ($\Sigma 2$ twins)*. This twinning does not occur systematically among the cases listed in Table 3.3.8.1, except for special metrical relations. Example: a primitive orthorhombic lattice with $b/a = \sqrt{3}$ and twin reflection plane (110) or $(\bar{1}10)$. The coincidence lattice is hexagonal with $a_{\text{hex}} = 2a$ and $[j] = 2$.

(iii) *Twins with $[j] = 3$ ($\Sigma 3$ twins)*. Twins with $[j] = 3$ are very common among rhombohedral and cubic crystals (*‘spinel law’*) with the following two representative twin operations:

(a) twofold rotation around a threefold symmetry axis $[111]$ (cubic or rhombohedral coordinate axes) or $[001]$ (hexagonal axes);

(b) reflection across the plane (111) or (0001) normal to a threefold symmetry axis.

Both twin operations belong to the same twin law if the crystal is centrosymmetric. Well known examples are the (0001) contact twins of calcite, the penetration twins of iron borate, FeBO_3 , with the calcite structure, and the spinel twins of cubic crystals (*cf.* Examples 3.3.6.6, 3.3.6.7 and Figs. 3.3.6.6–3.3.6.8). For crystals with a rhombohedral (R) lattice, the coincidence lattice is the primitive hexagonal (P) sublattice (whose unit cell is commonly used for the hexagonal description of rhombohedral crystals). Here, the two centring points inside the triple hexagonal R cell do not belong to the coincidence sublattice which is, hence, of index $[j] = 3$. The same holds for the spinel twins of cubic crystals, provided only one of the four threefold axes is involved in the twinning. For further details see Section 3.3.11.4.

(iv) *Twins with $[j] > 3$ ($\Sigma > 3$ twins)*. Whereas twins with $[j] = 3$ are very common and of high importance among minerals and metals, twins with higher lattice indices occur hardly at all. All these ‘high-index’ twins can occur systematically only in tetragonal, hexagonal, rhombohedral and cubic crystals, due to the geometric perpendicularity relations set out in Table 3.3.8.1. Note that for special lattice metrics (axial ratios and angles) they can occur, of course, in any crystal system. These special metrics, however, are not enforced by the crystal symmetry and hence the coincidences are not strict, but only ‘pseudo-coincidences’. $\Sigma 5$ and $\Sigma 7$ twins are treated in Section 3.3.11.4 and in Klapper & Hahn (2012).

Examples

(1) Tetragonal twins with twin reflection planes $\{120\}$ or $\{310\}$, or twofold twin axes $\langle 120 \rangle$ or $\langle 310 \rangle$ lead to $[j] = 5$, the largest value of $[j]$ that has been found so far for tetragonal twins. The coincidence lattice is again tetragonal with $\mathbf{a}' = 2\mathbf{a} + \mathbf{b}$,

3.3. TWINNING OF CRYSTALS

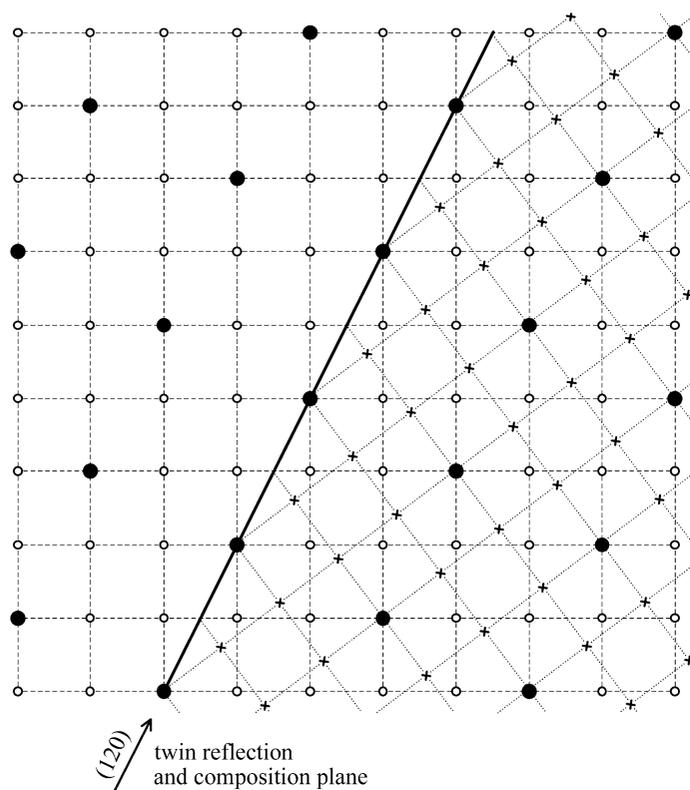


Fig. 3.3.8.1. Lattice relations of $\Sigma 5$ twins of tetragonal crystals with primitive lattice: twin mirror plane and composition plane (120) with twin displacement vector $\mathbf{t} = \mathbf{0}$. Small circles: lattice points of domain 1; small x: lattice points of domain 2; large black dots: $\Sigma 5$ coincidence sublattice.

$\mathbf{b}' = -\mathbf{a} + 2\mathbf{b}$, $\mathbf{c}' = \mathbf{c}$ and is shown in Fig. 3.3.8.1. An actual example, $\text{SmS}_{1.9}$ (Tamazyan *et al.*, 2000b), is discussed in Section 3.3.9.2.4.

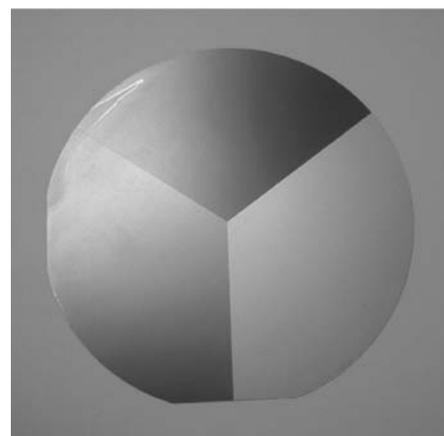
(2) There exist several old and still unsubstantiated indications for a $[j] = 5$ cubic garnet twin with twin reflection plane (210), *cf.* Arzruni (1887); Tschermak & Becke (1915, p. 594).

(3) *Klockmannite*, CuSe (Taylor & Underwood, 1960; Takeda & Donnay, 1965). This hexagonal mineral seems to be the only example for a hexagonal twin with $[j] > 3$. X-ray diffraction experiments indicate a reflection twin on (1340), corresponding to $[j] = 13$. Later structural studies, however, suggest the possibility of disorder instead of twinning.

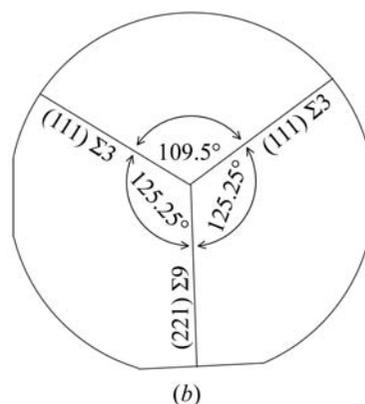
(4) *Galena*, PbS (NaCl structure). Galena crystals from various localities often exhibit lamellae parallel to the planes $\{441\}$ which are interpreted as (441) reflection twins with $[j] = 33$ ($\Sigma 33$ twin). These natural twins are deformation and not growth twins. In laboratory deformation experiments, however, these twins could not be generated. A detailed analysis of twinning in PbS with respect to plastic deformation is given by Seifert (1928).

(5) For cubic metals and alloys *annealing twins* (*recrystallization twins*) with $[j] > 3$ are common. Among them *high-order twins* (*high-generation twins*) are particularly frequent. They are based on the $\Sigma 3$ (spinel) twins (first generation) which may coalesce and form 'new twins' with $\Sigma 9 = 3^2$ [second generation, with twin reflection plane (221)], $\Sigma 27 = 3^3$ [third generation, twin reflection plane (115)], $\Sigma 81 = 3^4$ [fourth generation, twin reflection plane (447)] *etc.* Every step to a higher generation increases Σ by a factor of three (Gottstein, 1984). An interesting and actual example is the artificial silicon *tricrystal* shown in Fig. 3.3.8.2, which contains three components related by two (111) reflection planes (first generation, two $\Sigma 3$ boundaries) and one (221) reflection plane (second generation, one $\Sigma 9$ boundary).

(6) The same type of tricrystal has been found in cubic magnetite (Fe_3O_4) nanocrystals grown from the biogenic action



(a)



(b)

Fig. 3.3.8.2. (a) A (110) silicon slice (10 cm diameter, 0.3 mm thick), cut from a Czochralski-grown tricrystal for solar-cell applications. As seed crystal, a cylinder of three coalesced Si single-crystal sectors in (111) and (221) reflection-twin positions was used. Pulling direction [110] (Courtesy of M. Krühler, Siemens AG, München). (b) Sketch of the tricrystal wafer showing the twin relations [twin laws $m(111)$ and $m(221)$] and the Σ characters of the three domain pairs. The atomic structures of these (111) and (221) twin boundaries are discussed by Kohn (1956, 1958), Hornstra (1959, 1960) and Queisser (1963).

of magnetotactic bacteria in an aquatic environment (Devouard *et al.*, 1998). Here, HRTEM micrographs (Fig. 6 of the paper) show the same triple-twin arrangement as in the Si tricrystal above. The authors illustrate this triple twin by (111) spinel-type intergrowth of three octahedra exhibiting two $\Sigma 3$ and one $\Sigma 9$ domain pairs. The two $\Sigma 3$ interfaces are (111) twin reflection planes, whereas the $\Sigma 9$ boundary is very irregular and not a compatible planar (221) interface (*i.e.* not a twin reflection plane).

(7) A third instructive example is provided by the fivefold cyclic 'cozonal' twins (zone axis [110]) of Ge nanocrystals (Neumann *et al.*, 1996; Hofmeister, 1998), which are treated in Section 3.3.10.6.5 and Fig. 3.3.10.11. All five boundaries between neighbouring domains (sector angles 70.5°) are of the $\Sigma 3(111)$ type. Second nearest ($2 \times 70.5^\circ$), third nearest ($3 \times 70.5^\circ$) and fourth nearest ($4 \times 70.5^\circ$) neighbours exhibit $\Sigma 9$, $\Sigma 27$ and $\Sigma 81$ coincidence relations (second, third and fourth Σ generation), respectively, as introduced above in (5). These relations can be described by the 'cozonal' twin reflection planes (111), (221), (115) and (447). Since $5 \times 70.5^\circ = 352.5^\circ$, an angular gap of 7.5° would result. In actual crystals this gap is compensated by stacking faults as shown in Fig. 3.3.10.11. A detailed treatment of all these cases, including structural models of the interfaces, is given by Neumann *et al.* (1996).

(8) Examples of (hypothetical) twins with $[j] > 1$ due to metrical specialization of the lattice are presented by Koch (2004).

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

3.3.8.4. Approximate (pseudo-)coincidences of two or more lattices

In part (iv) of Section 3.3.8.2, three-dimensional lattice coincidences and twin lattices (sublattices) were considered under two restrictions:

(a) the lattice coincidences (according to the twin lattice index $[j]$) are *exact* (not approximate);

(b) only *two* lattices are superimposed to form the twin lattice.

In the present section these two conditions are relaxed as follows:

(1) In addition to exact lattice coincidences (as they occur for all merohedral twins) *approximate* lattice coincidences (pseudo-coincidences) are taken into account.

In this context, it is important to explain the meaning of the terms *approximate lattice coincidences* or *pseudo lattice coincidences* as used in this section. Superposition of two or more equal lattices (with a common origin) that are slightly misoriented with respect to each other leads to a three-dimensional moiré pattern of coincidences and anti-coincidences. The *beat period* of this pattern increases with decreasing misorientation. It appears sensible to use the term approximate or pseudo-coincidences only if the ‘splitting’ of lattice points is small within a sufficiently large region around the common origin of the two lattices. Special cases occur for reflection twins and rotation twins of pseudosymmetrical lattices. For the former, exact two-dimensional coincidences exist parallel to the (rational) twin reflection plane and the moiré pattern is only one-dimensional in the direction normal to this plane. Hence, the region of ‘small splitting’ is a two-dimensional (infinitely extended) thin layer of the twin lattice on both sides of the twin reflection plane [example: pseudo-monoclinic albite (010) reflection twins]. For rotation twins, the region of ‘small splitting’ is an (infinitely long) cylinder around the twin axis. On the axis the lattice points coincide exactly.

In general, a typical measure of this region, in terms of the reciprocal lattice, could be the size of a conventional X-ray diffraction photograph or a two-dimensional detector. Whereas the slightest deviations from exact coincidence lead to pseudo-coincidences, the ‘upper limit of the splitting’, up to which two lattices are considered as pseudo-coincident, is not definable on physical grounds and thus is a matter of convention and personal preference. As an angular measure of the splitting the *twin obliquity* has been introduced by Friedel (1926). This concept and its use in twinning will be discussed below in Section 3.3.8.5.

(2) The previous treatment of superposition of only two lattices is extended to multiple twins with several interpenetrating lattices which are related by a pseudo n -fold twin axis. Such a twin axis cannot be ‘exact’, no matter how close its rotation angle comes to the exact angular value. For this reason, twin axes of order $n > 2$ necessarily lead to *pseudo* lattice coincidences.

Here it is assumed that such pseudo-coincidences exist for any pair of neighbouring twin domains. As a consequence, pseudo-coincidences occur for all n domains. For this case, the following rules exist:

(i) Only n -fold twin axes with the crystallographic values $n = 3, 4$ and 6 lead to pseudo lattice coincidences of all domains. Example: cyclic triplets of aragonite (Fig. 3.3.2.4).

(ii) The number of (interpenetrating) lattices equals the number of different domain states [cf. Section 3.3.4.4(iii)], viz.

6, 3 or 2 lattices for $n = 6$,

3 lattices for $n = 3$,

4 or 2 lattices for $n = 4$,

whereby the case ‘2 lattices’ for $n = 6$ leads to exact lattice coincidence (merohedral twinning, e.g. Dauphiné twins of quartz).

(iii) There always exists *exact* (one-dimensional) coincidence of all lattice rows along the twin axis.

(iv) If there is a (rational) lattice plane normal to the twin axis, the splitting of the lattice points occurs only parallel to this plane. If, however, this lattice plane is pseudo-normal (i.e. slightly inclined) to the twin axis, the splitting of lattice points also has a small component along the twin axis.

3.3.8.5. Twin obliquity and lattice pseudosymmetry

The concept of *twin obliquity* has been introduced by Friedel (1926, p. 436) to characterize (metrical) pseudosymmetries of lattices and their relation to twinning. The obliquity ω is defined as the angle between the normal to a given lattice plane (hkl) and a lattice row $[uvw]$ that is not parallel to the (hkl) and, *vice versa*, as the angle between a given lattice row $[uvw]$ and the normal to a lattice plane (hkl) that is not perpendicular to $[uvw]$. The twin obliquity is thus a quantitative (angular) measure of the pseudosymmetry of a lattice and, hence, of the deviation which the twin lattice suffers in crossing the composition plane (cf. Section 3.3.8.1).

The smallest mesh of the net plane (hkl) together with the shortest translation period along $[uvw]$ define a unit cell of a sublattice of lattice index $[j]$; j may be $= 1$ or > 1 [cf. Section 3.3.8.2(iv)]. The quantities ω and j can be calculated for any lattice and any (hkl)/ $[uvw]$ combination by elementary formulae, as given by Friedel (1926, pp. 249–252) and by Donnay & Donnay (1972). A computer program has been written by Le Page (1999, 2002) which calculates for a given lattice all (hkl)/ $[uvw]$ / ω / j combinations up to given limits of ω and j . In the theory of Friedel and the French School, a (metrical) pseudosymmetry of a lattice or sublattice is assumed to exist if the twin obliquity ω as well as the twin lattice index j are ‘small’. This in turn means that the pair lattice plane (hkl)/lattice row $[uvw]$ is the better suited as twin elements (twin reflection plane/twofold twin axis) the smaller ω and j are.

The term ‘small’ obviously cannot be defined in physical terms. Its meaning rather depends on conventions and actual analyses of triperiodic twins. In his textbook, Friedel (1926, p. 437) quotes frequently observed twin obliquities of $3\text{--}4^\circ$ (albite $4^\circ 3'$, aragonite $3^\circ 44'$) with ‘rare exceptions’ of $5\text{--}6^\circ$. In a paper devoted to the quartz twins with ‘inclined axes’, Friedel (1923, pp. 84 and 86) accepts the La Gardette (Japanese) and the Esterel twins, both with large obliquities of $\omega = 5^\circ 27'$ and $\omega = 5^\circ 48'$, as pseudo-merohedral twins only because their lattice indices $[j] = 2$ and 3 are (*en revanche*) remarkably small. He considers $\omega = 6^\circ$ as a limit of acceptance [*limite prohibitive*; Friedel (1923, p. 88)].

Lattice indices $[j] = 3$ are very common (in cubic and rhombohedral crystals), $[j] = 5$ twins are rare and $[j] = 6$ seems to be the maximal value encountered in twinning (Friedel, 1926, pp. 449, 457–464; Donnay & Donnay, 1974, Table 1). In his quartz paper, Friedel (1923, p. 92) rejects all pseudo-merohedral quartz twins with $[j] \geq 4$ despite small ω values, and he points out, as proof that high j values are particularly unfavourable for twinning, that strictly merohedral quartz twins with $[j] = 7$ do not occur, i.e. that $\omega = 0$ cannot ‘compensate’ for high j values.

In agreement with all these results and later experiences (e.g. Le Page, 1999, 2002), we consider in Table 3.3.8.2 only lattice pseudosymmetries with $\omega \leq 6^\circ$ and $[j] \leq 6$, preferably $[j] \leq 3$. (It should be noted that, on purely mathematical grounds, arbitrarily small ω values can always be obtained for sufficiently large values of h, k, l and u, v, w , which would be meaningless for twinning.) The program by Le Page (1999, 2002) enables for the first time systematic calculations of many (‘all possible’) (hkl)/ $[uvw]$ combinations for a given lattice and, hence, statistical and geometrical evaluations of existing and particularly of (geometrically) ‘permissible’ but not observed twin laws. In Table 3.3.8.2, some examples are presented that bring out both the merits and the problems of lattice geometry for the theory of twinning. The

3.3. TWINNING OF CRYSTALS

Table 3.3.8.2. Examples of calculated obliquities ω and lattice indices $[j]$ for selected $(hkl)/[uvw]$ combinations and their relation to twinning

Calculations were performed with the program *OBLIQUE* written by Le Page (1999, 2002).

| Crystal | (hkl) | Pseudo-normal $[uvw]$ | Obliquity [°] | Lattice index $[j]$ | Remark |
|---|------------------------------------|-------------------------------|----------------------|------------------------|------------------------------------|
| Gypsum $A2/a$ $a = 6.51, b = 15.15, c = 6.28 \text{ \AA}$ $\beta = 127.5^\circ$ | (100) | [302] [805] | 2.47 0.42 | 3 4 | Dovetail twin (very frequent) |
| | (001) | [203] [305] | 5.92 0.95 | 3 5 | Montmartre twin (less frequent) |
| | (101) | [101] | 2.60 | 2 | No twin |
| | (11 $\bar{1}$) | [31 $\bar{4}$] | 1.35 | 4 | No twin |
| Rutile $P4_2/mnm$ $a = 4.5933, c = 2.9592 \text{ \AA}$ | (101) | [102] [307] | 5.02 0.84 | 3 5 | Frequent twin |
| | (301) | [101] | 5.43 | 2 | Rare twin |
| | (201) | [304] | 2.85 | 5 | No twin |
| | (210) or (130) | [210] or [130] | 0 | 5 | No twin |
| Quartz $P3_121$ $a = 4.9031, c = 5.3967 \text{ \AA}$ | (11 $\bar{2}$) | [111] | 5.49 | 2 | Japanese twin (La Gardette) (rare) |
| | (10 $\bar{1}$) | [211] | 5.76 | 3 | Esterel twin (rare) |
| | (10 $\bar{1}$) | [212] | 5.76 | 3 | Sardinia twin (very rare) |
| | (21 $\bar{3}$) or (14 $\bar{5}$) | [540] or [230] | 0 | 7 | No twin |
| Staurolite $C2/m$ $a = 7.871, b = 16.620, c = 5.656 \text{ \AA}$ $\beta = 90.00^\circ$ | (031) | [013] | 1.19 | 6 | 90° twin (rare) |
| | (231) | [313] | 0.90 | 12 | 60° twin (frequent) |
| | (201) | [101] | 0.87 | 3 | No twin |
| | (101) | [102] | 0.87 | 3 | No twin |
| Calcite $R\bar{3}c$ $a = 4.989, c = 17.062 \text{ \AA}$ [hexagonal axes, structural X-ray cell; cf. Section 3.3.10.2.2, Example (5)] | (01 $\bar{1}$) | [5.10.1] [7.14.2] [481] | 5.31 2.57 0.59 | 2 3 5 | No twin |
| | (10 $\bar{1}$) | [421] | 0.74 | 4 | Rare deformation twin (r-twin) |
| | (01 $\bar{1}$) | [121] | 0.59 | 5 | Frequent deformation twin (e-twin) |
| | (10 $\bar{1}$) | [14.7.1] | 1.54 | 5 | No twin |

'permissibility criteria' $\omega \leq 6^\circ$ and $[j] \leq 6$, mentioned above, are observed for most cases.

The following comments on these data should be made.

Gypsum: The calculations result in about 70 'permissible' $(hkl)/[uvw]$ combinations. For the very common (100) dovetail twin, four (100)/ $[uvw]$ combinations are obtained. Only the two combinations with smallest ω and $[j]$ are listed in the table; similarly for the less common (001) Montmartre twin. In addition, two cases of low-index (hkl) planes with small obliquities and small lattice indices are listed, for which twinning has never been observed.

Rutile: Here nearly twenty 'permissible' $(hkl)/[uvw]$ combinations with $\omega \leq 6^\circ$, $[j] \leq 6$ occur. For the frequent (101) reflection twins, five permissible cases are calculated, of which two are given in the table. For the rare (301) reflection twins, only the one case listed, with high obliquity $\omega = 5.4^\circ$, is permissible. For the further two cases of low obliquity and lattice index [5], twins are not known. Among them is one case of (strict) 'reticular merohedry', (210) or (130), with $\omega = 0$ and $[j] = 5$ (cf. Fig. 3.3.8.1).

Quartz: The various quartz twins with inclined axes were studied extensively by Friedel (1923). The two most frequent cases, the Japanese (11 $\bar{2}$) twin (called La Gardette twin by Friedel) and the (10 $\bar{1}$) Esterel twin, are considered here. In both cases, several lattice pseudosymmetries occur. Following Friedel, those with the smallest lattice index but relatively high obliquity close to 6° are listed in the table. Again, a twin of (strict) 'reticular merohedry' with $\omega = 0$ and $[j] = 7$ does not occur [cf. Section 3.3.9.2.3, Example (2)].

Staurolite: Both twin laws occurring in nature, (031) and (231), exhibit small obliquities but rather high lattice indices [6] and [12]. The frequent (231) 60° twin with $[j] = 12$ falls far outside the 'permissible' range. The further two planes listed in the table, (201) and (101), exhibit favourably small obliquities and lattice

indices, but do not form twins. The existing (031) and (231) twins of staurolite are discussed again in Section 3.3.9.2 under the aspect of 'reticular pseudo-merohedry'.

Calcite: For calcite, 19 lattice pseudosymmetries obeying Friedel's 'permissible criteria' are calculated. Again, only a few are mentioned here (indices referred to the structural cell). For the primary deformation twin (01 $\bar{1}$), e-twin after Bueble & Schmahl (1999), cf. Section 3.3.10.2.2, Example (5), one permissible lattice pseudosymmetry with small obliquity 0.59 but high lattice index [5] is found. For the less frequent secondary deformation twin (10 $\bar{1}$), r-twin, the situation is similar. The planes (01 $\bar{1}$) and (10 $\bar{1}$) permit small obliquities and lattice indices $\leq [5]$, but do not appear as twin planes.

The discussion of the examples in Table 3.3.8.2 shows that, with one exception [staurolite (231) twin], the obliquities and lattice indices of common twins fall within the $\omega/[j]$ limits accepted for lattice pseudosymmetry. Three aspects, however, have to be critically evaluated:

(i) For most of the lattice planes (hkl) , several pseudo-normal rows $[uvw]$ with different values of ω and $[j]$ within the $6^\circ/[6]$ limit occur, and *vice versa*. Friedel (1923) discussed this in his theory of quartz twinning. He considers the $(hkl)/[uvw]$ combination with the smallest lattice index as responsible for the observed twinning.

(ii) Among the examples given in the table, low-index $(hkl)/[uvw]$ combinations with more favourable $\omega/[j]$ values than for the existing twins can be found that never form twins. A prediction of twins on the basis of 'lattice control' alone, characterized by low ω and $[j]$ values, would fail in these cases.

(iii) All examples in the table were derived solely from lattice geometry, none from structural relations or other physical factors.

Note. As a mathematical alternative to the term 'obliquity', another more general measure of the deviation suffered by the

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

twin lattice in crossing the twin boundary was presented by Santoro (1974, equation 36). This measure is the difference between the metric tensors of lattice 1 and of lattice 2, the latter after retransformation by the existing or assumed twin operation (or more general orientation operation).

3.3.8.6. *Twinning of isostructural crystals*

In the present section, the critical discussion of the lattice theory of twinning is extended from the individual crystal species, treated in Section 3.3.8.5, to the occurrence of *merohedral twinning* in series of *isotypic* and *homeotypic crystals*. The crystals in each series have the same (or closely related) structure, space group, lattice type and lattice coincidences. The following cases are of interest here:

(i) Quartz (SiO_2), quartz-homeotypic gallium phosphate (GaPO_4) and benzil [$(\text{C}_6\text{H}_5\text{CO})_2$, so-called ‘organic quartz’] crystallize under normal conditions in the enantiomorphic space groups $P3_121$ and $P3_221$. In quartz, merohedral Dauphiné and Brazil $\Sigma 1$ twins are very frequent, whereas twins of the Leydolt (or ‘combined’) law are very rare (*cf.* Example 3.3.6.4). In gallium phosphate, Leydolt twins occur as frequently as Dauphiné and Brazil twins (Engel *et al.*, 1989). In benzil crystals, however, these twins are never observed, although the same space-group symmetries and conditions for systematic lattice coincidences as in quartz and in gallium phosphate exist. The reason is the completely different structure and chemical bonding of benzil, which is not capable of forming low-energy boundaries for these three twin laws.

(ii) Iron borate FeBO_3 , calcite CaCO_3 and sodium nitrate NaNO_3 crystallize under normal conditions in the calcite structure with space group $R32/c$. The rhombohedral lattice allows twinning with a hexagonal $\Sigma 3$ coincidence lattice (*cf.* Example 3.3.6.6). Practically all spontaneously nucleated FeBO_3 crystals grown from vapour (chemical transport) or solution (flux) are $\Sigma 3$ -twinned and form intergrowths of reverse and obverse rhombohedra (penetration twins). This kind of twinning is comparatively rare in calcite, where the twins usually appear with another morphology [contact twins on (0001)]. Interestingly, this $\Sigma 3$ twinning does not occur (or is extremely rare) in sodium nitrate. This shows that even for isotypic crystals, the tendency to form $\Sigma 3$ twins is extremely different. This can also be observed for crystals with the sodium chloride structure. Crystals of the silver halogenides AgCl and AgBr , precipitated from aqueous solution, develop multiple $\Sigma 3$ twins with high frequency (Bögels *et al.*, 1999), and so does galena PbS , whereas the isotypic alkali halogenides (*e.g.* NaCl , LiF) practically never (or only extremely rarely) form $\Sigma 3$ twins.

(iii) Another instructive example is provided by the $\Sigma 3$ (111) spinel twins in the sphalerite (ZnS) structure of III–V and II–VI semiconductor crystals (*cf.* Example 3.3.6.7). In some of these compounds this kind of twinning is quite rare (*e.g.* in GaAs), but in others (*e.g.* InP , CdTe) it is very frequent. Gottschalk *et al.* (1978) have quantitatively shown that the ease and frequency of twin formation is governed by the (111) stacking-fault energy [which is the energy of the (111) twin boundary]. They have calculated the (111) stacking-fault energies of various III–V semiconductors, taking into account the different ionicities of the bonds. The results prove quantitatively that the frequency of the $\Sigma 3$ twin formation is correlated with the (111) boundary energy.

These examples corroborate the early observations of Cahn (1954, pp. 387–388). The present authors agree with his elegantly formulated conclusion, ‘that the fact that two substances are isostructural is but a slender guide to a possible similarity in their twinning behaviour’.

3.3.8.7. *Conclusions*

In conclusion, the *lattice theory of twinning*, presented in this section, can be summarized as follows:

(i) The lattice theory represents one of the first systematic theories of twinning; it is based on a clear and well defined concept and thus has found widespread acceptance, especially for the description, characterization and classification of ‘triperiodic’ (merohedral and pseudo-merohedral) twins.

(ii) The concept, however, is purely *geometrical* and has as its object a mathematical, not a physical, item, the *lattice*. It takes into account neither the crystal structure nor the orientation and energy of the twin interface. This deficit has been pointed out and critically discussed as early as 1905 by Mügge, and later by Burgers (1927, 1932), Heide (1928), Buerger (1945), Cahn (1954, Section 1.3), Hartman (1956) and Holser (1958, 1960); it is the major reason for the limitations of the theory and its low power of prediction for actual cases of twinning.

(iii) The relations between twinning and lattice (pseudo-) symmetries, however, become immediately obvious and are proven by many observations as soon as *structural pseudosymmetries* exist. Twinning is always facilitated if a real or hypothetical ‘parent structure’ exists from which the twin law and the interface can be derived. Here, the *lattice pseudosymmetry* appears as a necessary consequence of the *structural pseudosymmetry*, which usually involves only small deformations of the parent structure, resulting in small obliquities of twin planes and twin axes (which are symmetry elements of the parent structure) and, hence, in twin interfaces of low energy. These structural pseudosymmetries are the result either of actual or hypothetical phase transitions (domain structures, *cf.* Chapter 3.4) or of structural relationships to a high-symmetry ‘prototype’ structure, as explained in Section 3.3.7.2.

The importance of structural pseudosymmetries was emphasized as early as 1927 by Burgers. His statement (‘the possibility of the twinning must, therefore, be connected with a definite pseudo-symmetrical character of the structure of the untwinned crystal’), however, was seriously attacked by Friedel (1928): *La formation de la macle est totalement indifférente à la symétrie ou à la pseudo-symétrie de l’édifice cristallin ou des groupes d’atomes qui le constituent. Elle est due uniquement à la rencontre des symétries ou de pseudo-symétries dans les périodes (mailles, simples ou multiples) de cet édifice* (‘The formation of a twin is totally independent of the symmetry or pseudosymmetry of the crystal structure or the groups of atoms which build it. It is uniquely due to the presence of symmetries or pseudosymmetries of the lattice [simple or multiple unit cells] of the crystal’). In a reply to this paper, Burgers (1932) corroborates his previous criticism by the statement ‘that the fundamental cause of twinning must be looked for in the force relations in the immediate neighbourhood of the last-formed layer of the growing crystal’. In his view the (pseudo)symmetry of the simple or multiple lattice of a twinned crystal ‘is only another manifestation of a pseudo-symmetrical character of the structure of the untwinned crystal as a whole’.

(iv) On the other hand, twinning quite often occurs without recognizable structural pseudosymmetry, *e.g.* the (100) dovetail twins and the (001) Montmartre twins of gypsum, as well as the (101) and (301) reflection twins of rutile and some further examples listed in Table 3.3.8.2. In all these cases, it can be concluded that the lattice theory of twinning is not the suitable tool for the characterization and prediction of the twins; in the terminology of Friedel: the twins are not ‘triperiodic’ but only ‘diperiodic’ or ‘monoperiodic’.

3.3.9. *Twinning by merohedry and pseudo-merohedry*

We now resume the discussion of Section 3.3.8 on three-dimensional coincidence lattices and pseudo-coincidence lattices and apply it to actual cases of twinning, *i.e.* we treat in the present section *twinning by merohedry* (‘*macles par mériédrie*’) and *twinning by pseudo-merohedry* (‘*macles par pseudo-mériédrie*’),