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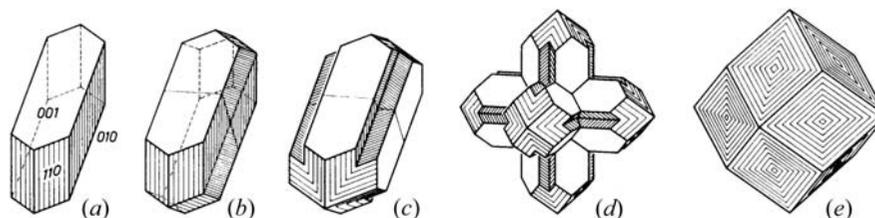

Fig. 3.3.6.16. The various steps (idealized) of phillipsite growth twins: (*a*) monoclinic untwinned, (*b*) orthorhombic, (*c*) tetragonal, (*d*) cubic, and (*e*) 'filled-in' pseudo rhomb-dodecahedron (after Ramdohr & Strunz, 1967, p. 754).

other, each with its own twin law. This may occur as a result of:

(1) two successive phase transitions, each with its own twinning scheme, or

(2) one phase transition with loss of two kinds of symmetry elements, or

(3) a phase transition superimposed on an existing growth twin.

Typical examples are:

(i) the cubic–tetragonal ($m\bar{3}m \Longleftrightarrow 4mm$) phase transition of BaTiO$_3$, described above. Here, 90° domains (due to the loss of the diagonal mirror planes) are superimposed by 180° domains (due to the loss of the inversion centres);

(ii) a similar case (tetragonal–monoclinic) is provided by the 'type case' of Henke (2003), (NO)$_2$VCl$_6$;

(iii) ammonium lithium sulfate exhibits pseudo-hexagonal growth-sector twins upon which lamellae of ferroelectric 180° domains are superimposed (Hildmann, 1980; Jennissen, 1990).

In this context, the term *complete twin* should be noted. It was coined by Curien & Donnay (1959) for the symmetry description of a crystal containing several merohedral twin laws. Their preferred example was quartz, but there are many relevant cases:

(i) The complete merohedral 'twins of twins' of quartz, *i.e.* the superposition of the Dauphiné, Brazil and Leydolt twins, can be formulated as follows:

$$\text{Dauphine twin law: } 321 \Rightarrow 6'(3)22'$$

$$\text{Brazil twin law: } 321 \Rightarrow \bar{3}'(3)2/m'1(\bar{1}')$$

$$\text{Leydolt twin law: } 321 \Rightarrow \bar{6}'(3)2m' = 3/m'2m'.$$

Combination = 'complete twin': $6'(3)/m'\,2/m'\,2'/m'(\bar{1}')$; this symmetry corresponds to the hexagonal holohedral point group $6/m\,2/m\,2/m$, *cf.* Example 3.3.6.4.

(ii) Another example is provided by KLiSO$_4$ (crystal class 6), extensively investigated by Klapper *et al.* (1987):

$$\text{Inversion twins: } 6 \Rightarrow 6/m'(\bar{1}')$$

$$\text{Reflection twins: } 6 \Rightarrow 6m'm'$$

$$\text{Rotation twins: } 6 \Rightarrow 62'2'.$$

Combination = 'complete twin': $6/m'2'/m'2'/m'(\bar{1}')$; this symmetry is isomorphic to the complete-twin symmetry of quartz, given above, and to the hexagonal holohedral point group $6/m\,2/m\,2/m$.

(iii) An example of a very extensive series of pseudo-merohedral *growth twins* is provided by the zeolite minerals phillipsite and harmotome (Hoffmann *et al.*, 1973). Both minerals are monoclinic, space group $P12/m1$ (Rinaldi *et al.*, 1974). The crystals occur in series of pseudo-merohedral growth twins as follows:

$$1\,2/m\,1 \rightarrow 2'/m'\,2/m\,2'/m' \rightarrow 4'/m'\,2/m\,2'/m' \rightarrow 4'/m'\,\bar{3}'\,2/m.$$

The total subgroup index [*i*] from the monoclinic to the cubic twin symmetry is stepwise $2 \times 2 \times 3 = 12$. These steps are illustrated in the sketches of Fig. 3.3.6.16. If the gaps between the interpenetrating domains are filled, as in Fig. 3.3.6.16(*e*), the twin appears as a pseudo-cubic rhomb-dodecahedron.

3.3.7. Genetic classification of twins

In Section 3.3.3, a classification of twins based on their morphological appearance was given. In the present section, twins are classified according to their origin. Genetic terms such as growth twins, transformation twins and mechanical twins were introduced by Buerger (1945) and are in widespread use. They refer to the *physical origin* of a given twin in contrast to its geometrical description in terms of a twin law. The latter can be the same for twins of different origin, but it will be seen that the generation of a twin has a strong influence on the shape and distribution of the twin domains. An extensive survey of the genesis of all possible twins is given by Cahn (1954).

3.3.7.1. *Growth twinning*

Growth twins can occur in nature (minerals), in technical processes or in the laboratory during growth from vapour, melt or solution. Two mechanisms of generation are possible for growth twins:

(i) formation during nucleation of the crystal;

(ii) formation during crystal growth.

3.3.7.1.1. *Twinning by nucleation*

In many cases, twins are formed during the first stages of spontaneous nucleation, possibly before the sub-critical nucleus reaches the critical size necessary for stable growth. This idea was originally proposed by Buerger (1945, p. 476) under the name *supersaturation twins*. There is strong evidence for twin formation during nucleation for penetration and sector twins, where all domains originate from one common well defined 'point' in the centre of the twinned crystal, which marks the location of the spontaneous nucleus.

Typical examples are the *penetration twins* of iron borate FeBO$_3$ (calcite structure), which are intergrowths of two rhombohedra, a reverse and an obverse one, and consist of 12 alternating twin domains belonging to two orientation states (see Example 3.3.6.6 and Fig. 3.3.6.6). Experimental details are presented by Klapper (1987) and Kotrbova *et al.* (1985). Further examples are the penetration twins of the spinel law (Example 3.3.6.7 and Fig. 3.3.6.8), the very interesting and complex [001] penetration twin of the monoclinic feldspar orthoclase (Fig. 3.3.7.1) and the *sector twins* of ammonium lithium sulfate with three orientation states (Fig. 3.3.7.2).

It should be emphasized that *all* iron borate crystals that are nucleated from flux or from vapour (chemical transport) exhibit penetration twinning. The occurrence of untwinned crystals has not been observed so far. Crystals of isostructural calcite and NaNO$_3$, on the other hand, do not exhibit penetration twins at all. In contrast, for ammonium lithium sulfate, NH$_4$LiSO$_4$, both sector-twinned and untwinned crystals occur in the same batch. In this case, the frequency of twin formation increases with higher supersaturation of the aqueous solution.
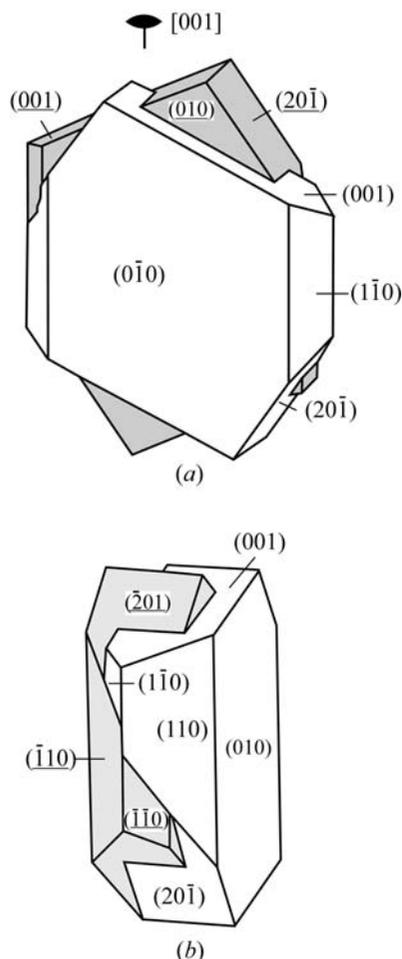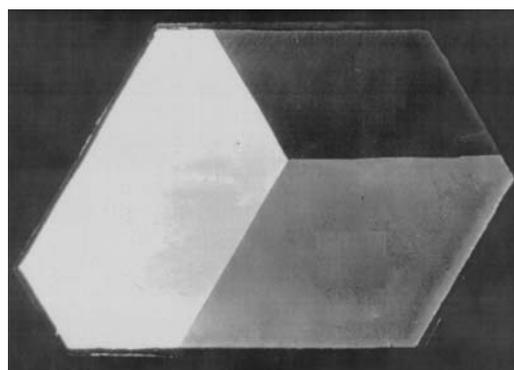
Fig. 3.3.7.1. Orthoclase (monoclinic K-feldspar). Two views, (*a*) and (*b*), of Carlsbad penetration twins (twofold twin axis [001]).

Fig. 3.3.7.2. Photographs of (001) plates ($\approx$ 20 mm diameter, $\approx$ 1 mm thick) of NH_4LiSO_4 between crossed polarizers, showing sector growth twins due to metric hexagonal pseudosymmetry of the orthorhombic lattice. (*a*) Nearly regular threefold sector twin (three orientation states, three twin components). (*b*) Irregular sector twin (three orientation states, but five twin components). After Hildmann (1980).
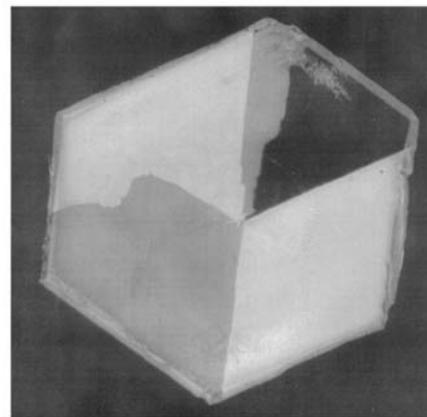
The formation of *contact twins* (such as the dovetail twins of gypsum) during nucleation also occurs frequently. This origin must always be assumed if both partners of the final twin have roughly the same size or if all spontaneously nucleated crystals in one batch are twinned. For example, all crystals of monoclinic lithium hydrogen succinate precipitated from aqueous solution form dovetail twins without exception.

The process of twin formation during nucleation, as well as the occurrence of twins only for specific members of isostructural series (*cf.* Section 3.3.8.6), are not yet clearly understood. A hypothesis advanced by Senechal (1980) proposes that the nucleus first formed has a symmetry that is not compatible with the lattice of the (macroscopic) crystal. This symmetry may even be noncrystallographic. It is assumed that, after the nucleus has reached a critical size beyond which the translation symmetry becomes decisive, the nucleus collapses into a twinned crystal with domains of lower symmetry. This theory implies that for nucleation-twinned crystals, a metastable modification with a structure different from that of the stable macroscopic state may exist for very small dimensions. For this interesting theoretical model no experimental proof is yet available, but it appears rather reasonable; as a possible candidate of this kind of genesis, the rutile 'eightling' in Example 3.3.6.10 (Figs. 3.3.6.11*d* and *i*) may be considered.

Recently, the ideas on twin nucleation have been experimentally substantiated by HRTEM investigations of multiple twins. The formation of these twins in nanocrystalline f.c.c. and diamond-type cubic materials, such as Ge, Ag and Ni, is explained by the postulation of various kinds of noncrystallographic nuclei, which subsequently 'collapse' into multiply twinned nanocrystals, *e.g.* fivefold twins of Ge; *cf.* Section 3.3.10.6.6. An extensive review is provided by Hofmeister (1998).

3.3.7.1.2. *Twinning during crystal growth*

(*a*) An alternative theory of twinning postulates the formation of a *two-dimensional nucleus* in twin position on a growth face of an existing macroscopic (previously untwinned) crystal. Such a mechanism was extensively described by Buerger (1945, pp. 472–475) and followed up by Menzer (1955) and Holser (1960). Obviously, this process is favoured by defects (inclusions, impurities) in the growth face. If the twin nucleus spreads out over the entire growth face, the twin boundary coincides with the growth face. This mechanism is generally assumed for the generation of large-area lamellar polysynthetic growth twins as observed for albite (Example 3.3.6.12 and Fig. 3.3.6.13). For a critical discussion of the origin of irrational twin interfaces in rotation twins such as the pericline twins see Cahn (1954, p. 408). It should be noted that this mechanism is possible only for twin boundaries of very low energy, since the boundary energy of the large interface has to be supplied in one step, *i.e.* during spreading out of one growth layer in twin position. It is obvious that this kind of twin formation can only occur if the twin boundary coincides with a prominent growth face (*F*-face, rarely *S*-face, according to Hartman, 1956).

(*b*) In the majority of growth twins, the twin boundary does *not coincide* with the growth face. This is the rule for merohedral twins, where the twin domains appear as 'inserts' in the shape of pyramids or lamellae extending from the initiating defects (mostly inclusions) into the direction of growth of the face on which the twin has started. Examples are the pyramid-shaped Brazil-twin inserts of quartz (Frondel, 1962, Fig. 61 on p. 87) and the lamellar stripes of growth twins of $KLiSO_4$ (Klapper *et al.*, 1987, especially Fig. 5). Similar pyramidal twin inserts are observed for Dauphiné growth twins in natural and synthetic

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quartz. These twin morphologies in quartz, however, are often considerably modified after growth by (partial) ferrobielastic switching of the domains, which is easily induced by stress at elevated temperatures [*cf.* Section 3.3.7.3(iii)]. Illustrations of such Dauphiné twins are given by Frondel (1962, Fig. 49 on p. 78).

The growth-twin inserts as described above appear improbable for non-merohedral twins because unfavourable high-energy boundaries would be involved. As a consequence, it must be concluded that non-merohedral twins with boundaries *not* coinciding with a (prominent) growth face (*e.g.* dovetail twins of gypsum) must form during the nucleation stage of the crystal (Section 3.3.7.1.1 above).

(*c*) Another model of twin formation has been suggested by Schaskolsky & Schubnikow (1933). It is based on the idea that in the melt or solution the pre-existing small crystals make accidental contact with analogous faces $(hkl)_1$ and $(hkl)_2$ parallel, rotate and *agglutinate in twin position*, and continue to grow as a twin. This concept is also favoured by Buerger (1960*b*). The model of Schaskolsky & Schubnikow is based on their interesting experiments with many ($\approx$ 1400) K-alum crystals (up to 0.5 mm in size), which sediment in solution on horizontal octahedron (111) and cube (100) faces of large alum crystals (20–30 mm in size). A statistical analysis of the orientation distribution of the sedimented crystals reveals a significantly increased frequency of (111)/(111) parallel intergrowths, of regular (001)/(111) intergrowths and of (111) spinel twins. The authors interpret this result as a rotation of the small crystals around the contact-face normal after deposition on the large crystal. This *initial contact plane* (ICP) model of twin formation was critically discussed by Senechal (1980) and considered as questionable, an opinion which is shared by the present authors.

(*d*) Finally, it is pointed out that twinning may drastically modify the regular *growth morphology* of (untwinned) crystals. A prominent example is the tabular shape of (111)-twinned cubic crystals with the large face parallel to the (111) contact plane. This is due to the increased lateral growth rate of the faces meeting in re-entrant edges (*re-entrant corner effect*; Hartman, 1956; Ming & Sunagawa, 1988). The (111) tabular shape of twinned cubic crystals plays an important role for photographic materials such as silver bromide, AgBr (Buerger, 1960*b*; Bögels *et al.*, 1997, 1998). A more extreme *habit modification* is exhibited by the ⟨110⟩ growth needles of cubic AgBr, which contain two {111} twin planes intersecting along ⟨110⟩ (Bögels *et al.*, 1999).

The phenomenon of habit modification by twinning has been developed further by Senechal (1976, 1980), who presents an alternative model of the genesis of penetration twins (*cf.* Section 3.3.7.1.1 above): initial cubic (111) contact twins consisting of two octahedra change their habit during growth so as to form two interpenetrating cubes of the spinel law. As a further example, chabasite is cited.

(*e*) During *melt growth* of the important cubic semiconductors with the diamond structure (Si, Ge) and sphalerite (zinc sulfide) structure (*e.g.* indium phosphide, InP), twins of the spinel law [twin mirror plane (111) or twofold twin axis [111], *cf.* Section 3.3.10.3.3] are frequently formed. Whereas this twinning is relatively rare and can easily be avoided for Si and Ge, it is a persistent problem for the III–V and II–VI compound semiconductors, especially for InP and CdTe crystals, which have a particularly low {111} stacking-fault energy (Gottschalk *et al.*, 1978). For Czochralsky growth, these twins are usually nucleated at 'edge facets' forming at the surface of the 'shoulder' (or 'cone region') where the growing crystal widens from the seed rod to its final diameter. Once nucleated, they proceed during further growth as bulk twins or, more frequently, as twin lamellae with sharp {111} contact planes. For a [111] pulling direction, the three equivalent {111} twin planes with inclination of 19.5° against the pull axis [111] are usually activated, whereas the perpendicular (111) twin plane does not occur, or only rarely occurs (Bonner,

1981; Tohno & Katsui, 1986). These twins can be avoided by optimizing the growth conditions, in particular by the choice of a proper cone angle, which is the most crucial parameter. A mechanism of the {111} twin formation of III–V compound semiconductors was suggested by Hurle (1995) and experimentally confirmed for InP, using synchroton-radiation topography combined with chemical etching and Nomarski microscopy, by Chung *et al.* (1998) and Dudley *et al.* (1998). A comprehensive X-ray topographic study of (111) twinning in indium phosphide crystals, grown by the liquid-encapsulated Czochralski technique, and its interaction with dislocations is presented by Tohno & Katsui (1986).

(*f*) It should be noted lastly that '*annealing twins*' (which are an important subject in metallurgy) are not treated in this section, because they are considered to be part of bicrystallography. These twins are formed during recrystallization and grain growth in annealed polycrystalline materials (*cf.* Cahn, 1954, pp. 399–401).

3.3.7.2. *Transformation twinning*

A solid-to-solid (polymorphic) phase transition is – as a rule – accompanied by a symmetry change. For displacive and order–disorder transitions, the symmetries of the 'parent phase' (prototype phase) $\mathcal{G}$ and of the 'daughter phase' (deformed phase) $\mathcal{H}$ exhibit frequently, but not always, a group–subgroup relation. During the transition to the low-symmetry phase the crystal usually splits into different domains. Three cases of transformation-twin domains are distinguished:

(i) The symmetry operations suppressed during the transition belong to the point group $\mathcal{G}$ of the high-symmetry (prototype) phase, whereas the lattice, except for a small affine deformation, is unchanged (*translationengleiche subgroup*). In this case, the structures of the domains have different orientations and/or different handedness, both of which are related by the suppressed symmetry elements. Thus, the transition induces twins with the suppressed symmetry elements acting as twin elements (twin law). The number of *orientation states* is equal to the index $[i] = |\mathcal{G}|/|\mathcal{H}|$ of the group–subgroup relation, *i.e.* to the number of cosets of $\mathcal{G}$ with respect to $\mathcal{H}$, including $\mathcal{H}$ itself; *cf.* Section 3.3.4.1. If, for example, a threefold symmetry axis is suppressed, three domain states related by approximate 120° rotations will occur (for the problems of pseudo-*n*-fold twin axes, see Section 3.3.2.3.2). A further well known example is the α–β phase transformation of quartz at 846 K. On cooling from the hexagonal β phase (point group 622) to the trigonal α phase (point group 32), the twofold rotation $2_z = 6^3$, contained in the sixfold axis of β-quartz, is suppressed, and so are the other five rotations of the coset (*cf.* Example 3.3.6.4.1). Consequently, two domain states appear (Dauphiné twins). These twins are usually described with the twofold axis along [001] as twin element.

(ii) If a lattice translation is suppressed without change of the point-group symmetry (*klassengleiche subgroup*), *i.e.* due to loss of cell centring or to doubling (tripling *etc.*) of a lattice parameter, *translation domains* (antiphase domains) are formed (*cf.* Wondratschek & Jeitschko, 1976). The suppressed translation appears as the fault vector of the *translation boundary* (antiphase boundary) between the domains. Recently, translation domains were called 'translation twins' (T-twins, Wadhawan, 1997, 2000), *cf.* Section 3.3.2.4, Note (7).

(iii) The two cases can occur together, *i.e.* point-group symmetry and translation symmetry are both reduced in one phase transition (*general subgroup*). Here caution in the counting of the number of domain states is advisable since now orientation states and translation states occur together.

Well known examples of ferroelastic transformation twins are K_2SO_4 (Example 3.3.6.8) and various perovskites (Example 3.3.6.14). Characteristic for non-merohedral (ferroelastic) trans-

formation twins are their planar twin boundaries and the many parallel (lamellar) twin domains of nearly equal size. In contrast, the twin boundaries of merohedral (non-ferroelastic) transformation twins, *e.g.* Dauphiné twins of quartz, often are curved, irregular and non-parallel.

Transformation twins are closely related to the topic of *Domain structures*, which is extensively treated by Janovec & Přívratská in Chapter 3.4 of this volume.

A generalization of the concept of transformation twins includes twinning due to structural relationships in a family of related compounds ('structural twins'). Here the parent phase is formed by the high-symmetry 'basic structure' ('aristotype') from which the 'deformed structures' and their twin laws, occurring in other compounds, can be derived by subgroup considerations similar to those for actual transformation twins. Well known families are ABX_3 ('perovskite tree', now often generalized as 'Bärnighausen tree'; Bärnighausen, 1980) and A_2BX_4 (Na$_2$SO$_4$- and K$_2$SO$_4$-type compounds). In Example (3) of Section 3.3.9.2.4, growth twins among MeX_2 dichalcogenides are described in detail.

3.3.7.3. *Mechanical twinning*

Under mechanical load, some crystals can be 'switched' – partly or completely – from one orientation state into another. This change frequently proceeds in steps by the switching of domains. As a rule, the new orientation is related to the original one by an operation that obeys the definition of a twin operation (*cf.* Section 3.3.2.3). In many cases, the formation of *mechanical twins* (German: *Druckzwillinge*) is an essential feature of the plasticity of crystals. The deformation connected with the switching is described by a homogeneous shear. The domain arrangement induced by mechanical switching is preserved after the mechanical load is released. In order to re-switch the domains, a mechanical stress of opposite sign (coercive stress) has to be applied. This leads to a *hysteresis* of the stress–strain relation. In many cases, however, switching cannot be repeated because the crystal is shattered.

All aspects of mechanical twinning are reviewed by Cahn (1954, Section 3). A comprehensive treatment is presented in the monograph *Mechanical Twinning of Crystals* by Klassen-Neklyudova (1964). A brief survey of mechanical twinning in metals is given by Barrett & Massalski (1966).

With respect to symmetry, three categories of mechanical twins are distinguished in this chapter:

(i) *Mechanical twinning in the 'traditional' sense*. This kind of twinning has been studied by mineralogists and metallurgists under the name *deformation twins* for a long time. Well known examples are the deformation twins of calcite, galena, chalcopyrite and cubic metals. The characteristic feature is the non-existence of a real or virtual *parent phase* with a *crystallographic supergroup*. From a symmetry point of view, this means that the composite symmetry of the twin is noncrystallographic [*cf.* Section 3.3.4.4(ii)]. This case is illustrated by the famous deformation twins of calcite (Fig. 3.3.7.3): The *eigensymmetry* $\mathcal{H}$ of calcite is $\bar{3}2/m$, and the most conspicuous twin element is the twin reflection plane $(01\bar{1}2)$ which is parallel to an edge of the cleavage rhombohedron $\{10\bar{1}1\}$. The extension of the *eigensymmetry* by this twin operation does not lead to a crystallographic composite symmetry, but the reduced composite symmetry is crystallographic, $\mathcal{K}^* = 2/m\,2/m\,2/m$.

Another famous case is that of the $\Sigma 3$ deformation twins of cubic metals that obey the spinel law of mineralogy [most conspicuous twin element: reflection plane parallel to (111)]. The extension of the *eigensymmetry* $4/m\,\bar{3}\,2/m$ by the twin operation leads to a noncrystallographic composite symmetry. The reduced composite symmetry $\mathcal{K}^*$, which is constructed from the intersection symmetry $\mathcal{H}^*$, however, is crystallographic (*cf.* Example 3.3.6.7).
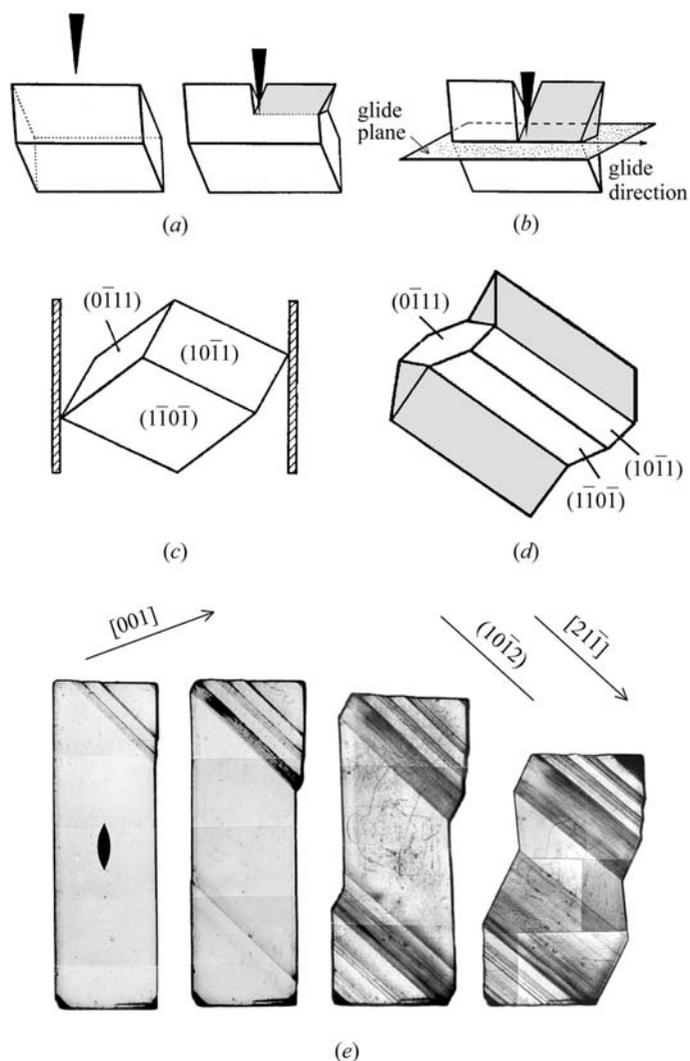

Fig. 3.3.7.3. Mechanical twins of calcite, CaCO$_3$. All indices refer to the standard morphological cell [*cf.* Section 3.3.10.2.2, Example (5)]. (*a*) Generation of a deformation twin by a knife-edge impact (after Baumhauer, 1879). (*b*) Description as a glide process ('twin glide') on plane $(01\bar{1}2)$. (*c*), (*d*) Generation of deformation twins by compression of the cleavage rhombohedron $\{10\bar{1}1\}$ (Mügge, 1883). The shaded twin components have the same orientation. (*e*) Successive stages of deformation twinning of NaNO$_3$ (isotypic with calcite) by uniaxial compression. The compression axis (vertical) is chosen with an angle of 45° against the twin glide plane $(10\bar{1}2)$ and the glide direction $[21\bar{1}]$. The direction of the twofold axis is shown in the left-hand figure. Original size of the sample: *ca.* $3 \times 3 \times \sim 9.5$ mm. Part (*e*) courtesy of H. E. Hoefer, PhD thesis, University of Cologne, 1989.

A description of the (plastic) deformation by twinning in terms of strain ellipsoids is presented in Section 3.3.10.1.

(ii) *Ferroelastic twinning*. In 1970, a special category of mechanical twins was introduced and characterized by Aizu (1970*a*), who also coined the term *ferroelasticity*. This group of twins had already been treated, as part of the mechanical twins, by Klassen-Neklyudova in her 1964 monograph mentioned above. The defining property of a ferroelastic crystal is the existence of a displacive (group–subgroup) transition, either real or virtual, from the parent phase into the ferroelastic phase with the essential requirement that parent and daughter phase belong to different crystal families. Only this symmetry feature allows for a *spontaneous shear strain* of the twin domains. The spontaneous deformations in a pair of domains have the same magnitude, but opposite signs. If the domain states can actually be switched into each other by a mechanical stress, the phase is called *ferroelastic*, otherwise it is called here *potentially ferroelastic*.

Ferroelastic twinning is not necessarily the result of a *real* phase transition. Switchable ferroelastic twins are frequently formed during growth. An example is orthorhombic ammonium

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sulfate, which can only be grown from aqueous solution and which frequently develops pseudohexagonal 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 modulus[4] 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 $YBa_2Cu_3O_{7-\delta}$ 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 $R\bar{3}c \longleftrightarrow R\bar{3}m$ 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)

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[4] Defined in Section 1.3.3.1.