3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

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 [(C$_6$H$_5$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 3.3.6.3). 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 $R\bar{3}2/c$. The rhombohedral lattice allows twinning with a hexagonal $\Sigma 3$ coincidence lattice (*cf.* Example 3.3.6.5). 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 3.3.6.6). 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 by 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 pseudo-symmetries* 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 pseudo-symmetry*, 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 3.3.9.2 below.

(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*'), both for lattice index $[j] = 1$ and $[j] > 1$, as introduced by Friedel (1926, p. 434). Often (strict) merohedral twins are called 'parallel-lattice twins' or 'twins with parallel axes'. Donnay & Donnay (1974) have introduced the terms *twinning by twin-lattice symmetry* (TLS) for merohedral twinning and *twinning by twin-lattice quasi-symmetry* (TLQS) for pseudo-merohedral twinning, but we shall use here the original terms introduced by Friedel.

3.3.9.1. *Definitions of merohedry*

In the context of twinning, the term 'merohedry' is applied with two different meanings which should be clearly distinguished in order to avoid confusion. The two cases are:

Case (1): '*Merohedry' of point groups*

A merohedral point group is a subgroup of the holohedral point group (lattice point group) of a given crystal system (crystal family), *i.e.* group and subgroup belong to the same crystal system. This is the original sense of the term *merohedry*, which has the morphological meaning of reduction of the number of faces of a given crystal form as compared with a *holohedral* crystal form. The degree of merohedry is given by the subgroup index $[i]$. For point groups within the same crystal family, possible indices $[i]$ are 2 (hemihedry), 4 (tetartohedry) and 8 (ogdohedry). The only example for $[i] = 8$ is the point group 3 in the hexagonal holohedry $6/m\,2/m\,2/m$.

If the point group of a crystal is reduced to such an extent that the subgroup belongs to a crystal family of lower symmetry, this subgroup is called a *pseudo-merohedral* point group, provided that the structural differences and, hence, also the metrical

references