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

A mechanical analogy to ferroelectric domains exists in the form of domains that differ in strain and can be switched by mechanical stress. This effect was studied under the name 'twinning with change of form' in the monoclinic ferroelectric phase of Rochelle salt by Klassen-Neklyudova *et al.* (1948) and Chernysheva (1950). A detailed description of this work in English is presented by Klassen-Neklyudova (1964, pp. 27–30, 75–78) in her monograph on mechanical twinning of crystals. Indenbom (1960) has shown that such behaviour is not confined to ferroelectric crystals and has listed many symmetry changes of potential phase transitions accompanied by the appearance of a spontaneous strain that could give rise to domains with different strain. Aizu (1969) called such crystals *ferroelastic crystals* in analogy with ferroelectric crystals. *Ferroelastic domains* differ in spontaneous strain and can be switched by mechanical stress.

Generalization of the concepts of ferromagnetic, ferroelectric and ferroelastic crystals followed soon after (Aizu, 1970): A *ferroic crystal* has two or more *orientation states* (oriented bulk structures of domains) that can be switched by means of a magnetic field, an electric field, a mechanical stress or by a combination of these. *Ferroic domains* are distinct in some tensors describing the material properties of the crystal. Aizu has also shown that the type of domain structure is determined by the change of point-group symmetry at the structural phase transition from a *prototypic* (*parent*, *high-symmetry*) *phase* without domains to a *ferroic* (*distorted*, *low-symmetry*, *daughter*) *phase* in which domains appear.

A more detailed history of the research of ferromagnetic, ferroelectric, ferroelastic and ferroic materials in general can be found in the book by Wadhawan (2000).

The domain structure determines to a certain extent electric, elastic, electromechanical and other properties of ferroic crystals. The investigation of domain structures has thus become an inseparable part of the research of ferroelectrics, ferroelastics and ferroic crystalline materials in general.

Most of the work has been devoted to ferroelectrics, since their specific properties have found important applications, some of which (*e.g.* production of anisotropic ceramics, ferroelectric memories) are based on irreversible and hysteretic changes of the ferroelectric domain structure under an electric field. References to ferroelectric, ferroelastic and other domain structures are given at the end of Section 3.4.1.

Even though the basic concepts of *twinning* and *domain structures* are closely related and have many aspects in common, the study of both subjects has developed independently, using different terms and symbols to describe rather similar facts. There are many cases that can be treated equally well by both approaches, *e.g.* merohedral twins and non-ferroelastic domain structures. There are cases, however, which can only be understood with one of the two concepts, *e.g.* the (111) spinel twins cannot be interpreted as a domain structure, because a high-symmetry parent phase does not exist. Of the two topics, twinning is the older, whereas the younger topic domain structure has recently advanced to a more detailed physical understanding.

In the two following chapters, 3.3 and 3.4, the two topics are treated separately and in their own right. It will be apparent that the two approaches, despite the great similarity of their objects, are quite different: for *domain structures* the all-important theoretical basis is the existence of a – real or potential (hypothetical) – *parent* (*prototypic*) *phase* from which the *ferroic* (*distorted*) *phase* is derived. This lowering of symmetry, expressed by a group–subgroup relation between the symmetries of the parent and ferroic phases, is the source of an impressive theoretical edifice which allows the explanation, and even the prediction, of many crystallographic properties of a given domain structure.

The situation is different in *twinning*: whereas *transformation twins* are closely related to domain structures and hence can be treated with the same theoretical tools, many *growth twins* and *mechanical twins* are characterized by the absence of an existing – and even a hypothetical – parent structure. From this it follows that growth and mechanical twins (which are the typical twin specimens of mineral collections) are to a much lesser extent amenable to group-theoretical analysis. Instead, each twinning case must be considered separately, and the orientation and contact relations of the twin partners must be individually ascertained. This requires discussion of many 'type cases'.

The present chapter continues with a short excursion into bicrystallography (Section 3.2.2), a topic not treated further in this article, followed by Section 3.2.3 with an exposition of basic concepts of set theory and group theory needed in Chapters 3.3 and 3.4.

3.2.2. A brief survey of bicrystallography

Both twinning and domain structures appear to be special cases of the relatively young research field of *bicrystallography* (Pond & Vlachavas, 1983), which has its origin in the study of *grain boundaries* in metals. Grains are coexisting crystals with identical composition and structure but with different orientations. Coexisting grains can be formally treated as generalized twins in which one of the conditions (*viz* a crystallographic relation between the twin components) is dropped.

A common feature of twins, domain structures and grain aggregates is the interface between coexisting crystals. The simplest edifice containing a crystalline interface is a bicrystal consisting of two semi-infinite perfect crystals (components) and a single planar interface along which the two crystals adjoin. For easier comprehension, one crystal of a bicrystal can be 'coloured' black and the other crystal white. Then the operations that leave both crystals unchanged are trivial colour-preserving symmetry operations, whereas the *symmetrizing operations*, which transform the black crystal into the white one and *vice versa*, are nontrivial colour-reversing operations. If one marks these colour-reversing operations by a prime or a star, then the symmetry group of a bicrystal has the structure of a *dichromatic* (*black-and-white*) *group* (see Section 3.2.3.2.7).

The dissymmetrization (symmetry reduction or lowering, symmetry descent) plays a basic role in bicrystallography. This is a process in which an object changes from a high-symmetry form into a low-symmetry form. As shown in Chapter 3.4, any dissymmetrization is accompanied by the formation of several symmetrically equivalent specimens of the low symmetry called *variants*. Variants are related by suppressed (lost) symmetry operations that are present in the low-symmetry form but are missing in the high-symmetry form. The set of all low-symmetry variants recovers the symmetry of the high-symmetry form. This general statement is referred to as the *law of symmetry compensation* and can be alternatively expressed by the following sentence (Shubnikov & Koptsik, 1974): If symmetry is reduced at one structural level, it arises and is recovered at another structural level. A paradigmatic example of dissymmetrization is a structural phase transition in which a high-symmetry parent (prototypic) phase changes into a low-symmetry distorted (ferroic) phase. The variants of the low-symmetry distorted phase are called single domain states or orientation states. The set of all single domain states recovers the high symmetry of the parent phase (see Chapter 3.4).

A systematic method for deriving the bicrystal symmetry, which is identical with the symmetry of the bicrystal interface, consists of four hierarchical stages (Pond & Vlachavas, 1983). At each stage, the bicrystal is represented by a construct (model) which is more detailed – and has, therefore, the same or lower symmetry – than the construct of the previous stage. These successive dissymmetrizations bring about at each stage equivalent variants of the bicrystal's construct. Different sets of variants

at different stages have distinct physical significance and provide a basic generic classification of bicrystals and their interfaces.

The first stage deals with the so-called dichromatic pattern consisting of two interpenetrating black and white lattices of the two crystal components (Pond & Bollmann, 1979). The coinciding 'grey' points constitute the *coincidence site lattice* (CSL) (see Bollmann, 1970, 1982), which corresponds to the twin lattice in twinning (see Section 3.3.8). To find variants of the dichromatic pattern, bicrystallography replaces the symmetry group of a nonexistent previous 'zero stage' with a minimal group containing symmetries of the black crystal and the white crystal. This group is called the *embracing* or *fundamental group of dichromatic patterns* (Shubnikov & Koptsik, 1974; Pond & Vlachavas, 1983; Wadhawan, 2000). If the symmetry group of the dichromatic pattern is smaller than the embracing group, then this dissymmetrization produces orientational or translational variants of the dichromatic pattern.

In the second stage, black and white lattices are decorated by atoms and these crystal structures are represented by lattice complexes. [A lattice complex of a crystal is here defined as the set of points obtained by carrying out on each occupied atomic position all symmetry operations of the crystal's space group. Note that in crystallography the term 'lattice complex' has a different meaning; see *IT* A (2005), Parts 8 and 14.] Two interpenetrating black and white lattice complexes of crystal components form the dichromatic complex of a bicrystal. If the symmetry of the dichromatic complex is lower than that of the dichromatic pattern, the dissymmetrization gives rise to complex variants of the dichromatic complex. The concept of a dichromatic complex corresponds to the concept of a domain pair in domain structure analysis (see Section 3.4.3).

Mental constructions of the first two stages specify only the relation between the lattices and structures of crystal components of a bicrystal. In the third stage, an *ideal bicrystal* is formed by sectioning the black-and-white lattice (or structure) on the interface plane and discarding the black lattice (or structure) on one side of the section and the white lattice (structure) on the other side. If the interfacial plane is a crystallographic plane with two-dimensional periodicity, then the symmetry of this ideal bicrystal is described by a *dichromatic layer group* (see Sections 3.4.4.2 and 3.4.4.3). This group is smaller than the space-group symmetry of the dichromatic complex and this dissymmetrization gives rise to *morphological variants* of the ideal bicrystal. Operations suppressed at this dissymmetrization relate different morphological variants of the ideal bicrystal. An ideal bicrystal corresponds to a domain twin with zero-thickness domain wall (see Section 3.4.4).

All three preceding stages use geometrical models of an interface with fixed atomic positions. At the final fourth stage, these geometrical constraints are lifted and the ideal bicrystal relaxes to a *real* or *relaxed bicrystal* with a minimum free energy. During this relaxation process the interface plane may migrate into either crystal, one crystal may translate rigidly with respect to the other, and each atom may adjust its position to relax any resultant force acting on it. The relaxation may even include insertion or removal of additional material at the interface. If the symmetry of the relaxed bicrystal is lower than that of the ideal bicrystal, then relaxational variants of the relaxed bicrystal appear. The one-dimensional interface between two interfacial relaxational variants forms a line defect of the bicrystal interface. Relaxation variants of finite-thickness domain walls and line defects in these walls are discussed in Section 3.4.4.

Two main theoretical approaches have been used in examining the microscopic structure of a real bicrystal interface. In the older one, a real interface is treated as a *periodic array of dislocations*. This approach, still based on geometrical models, has explained successfully the microscopic structure of small-angle grain boundaries, but has failed in large-angle grain boundaries (misorientation angle larger than $15°$).

More recent investigations utilizing computer simulations allow one to lift geometrical constraints and permit the calculation of equilibrium atomic positions directly from interatomic forces. These calculations have revealed that the lattice coincidence is almost always lost upon relaxation and that the microscopic structure of bicrystal interfaces can be described as an ordered sequence of coordination polyhedra. These conclusions have been confirmed by high-resolution electron microscopy. For more details see, for example, Fischmeister (1985), Sutton & Balluffi (1995) and Gottstein & Shvindlerman (1999).

The first three 'classical' stages of the bicrystallographical analysis already yield valuable conclusions. They disclose generic relations between different interfaces, specify crystallographically equivalent variants of an interface and classify line defects in interfaces. The symmetry of a bicrystal imposes constraints on tensor properties of the bicrystal interface, provides classification of the interfacial vibrational modes, discloses possible interfacial transitions *etc.* (see, for example, Kalonji, 1985).

The methodology of bicrystallography has many common features with the symmetry analysis of domain structures but, since both approaches have developed independently, they use a different terminology. Moreover, in comparison with bicrystals, domain structures and twins are more restricted by crystallographic constraints. This has resulted in more extensive application of group theory in domain structures than in bicrystallography. On the other hand, bicrystallography is more general and can even treat interfaces between two crystals belonging to different phases (heterophase interfaces).

A synoptic 'roadmap for the use of interfacial symmetry', compiled by Kalonji (1985), provides a quick guide to the possible applications of bicrystallography. A short introduction to bicrystallography can be found in Wadhawan (2000); a brief comparison of the concepts and terminologies of bicrystals, twins and domain structures is presented by Hahn *et al.* (1999). An extensive treatment of bicrystallography is available in the paper by Pond & Vlachavas (1983) and in the book by Sutton & Balluffi (1995), where other aspects of crystalline interfaces are also thoroughly covered.

3.2.3. Mathematical tools

Analysis of domain structures and twins does not deal primarily with single-crystal structures, as does classical crystallography, but studies collections of several crystal structures – which usually differ in orientation and position in space – and examines relations between these structures and their coexistence. The exact formulation of such an analysis uses mathematical concepts that are not yet quite common in crystallography. Thus, *e.g.*, a collection of crystallographic objects has to be decomposed into equivalence classes called orbits and strata, or the symmetry of an object (structure, domain wall, twin) has to be described with respect to a given group, which necessitates replacing the usual notion of a symmetry group by a 'stabilizer' (isotropy group). A prerequisite of introducing these terms is the concept of group action, which provides a basic and efficient tool for domain-structure analysis.

Another special feature of domain studies is that one can associate with a ferroic structure under study another structure, called the parent (prototypic) structure, from which the ferroic structure can be derived by small microscopic distortions. The fact that the symmetry of the ferroic phase is lower than that of the parent phase invokes the notion of a subgroup. Associated notions such as conjugate subgroups, normalizers and decomposition of a group into left and double cosets of a subgroup play an important role in the analysis.

Since some of these concepts are not available in standard texts, we present in this section the necessary mathematical

references