

3.2. Twinning and domain structures

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3.2.1. Introduction and history

Twins have been known for as long as mankind has collected minerals, admired their beauty and displayed them in museums and mineral collections. In particular, large specimens of contact and penetration twins with their characteristic re-entrant angles and simulated higher symmetries have caught the attention of mineral collectors, miners and scientists. *Twinning* as a special feature of crystal morphology, therefore, is a ‘child’ of mineralogy, and the terms and symbols in use for twinned crystals have developed during several centuries together with the development of mineralogy.

The first scientific description of *twinning*, based on the observation of re-entrant angles, goes back to Romé de l’Isle (1783). Haüy (1801) introduced symmetry considerations into twinning. He described *hemitropes* (twofold rotation twins) and *penetration twins*, and stated that the *twin face* is parallel to a possible crystal face. Much pioneering work was done by Weiss (1809, 1814, 1817/1818) and Mohs (1822/1824, 1823), who extended the symmetry laws of twinning and analysed the symmetry relations of many twins occurring in minerals. Naumann (1830) was the first to distinguish between twins with parallel axes (*Zwillinge mit parallelen Achsensystemen*) and twins with inclined (*crossed*) axes (*Zwillinge mit gekreuzten Achsensystemen*), and developed the mathematical theory of twins (Naumann, 1856). A comprehensive survey of the development of the concept and understanding of twinning up to 1869 is presented by Klein (1869).

At the beginning of the 20th century, several important mineralogical schools developed new and far-reaching ideas on twinning. The French school of Mallard (1879) and Friedel (1904) applied the lattice concept of Bravais to twinning. This culminated in the lattice classification of twins by Friedel (1904, 1926) and his introduction of the terms *macles par méridrie* (twinning by merohedry), *macles par pseudo-méridrie* (twinning by pseudo-merohedry), *macles par méridrie réticulaire* [twinning by reticular (lattice) merohedry] and *macles par pseudo-méridrie réticulaire* (twinning by reticular pseudo-merohedry). This concept of twinning was very soon taken up and further developed by Niggli in Zürich, especially in his textbooks (1919, 1920, 1924, 1941). The lattice theory of Mallard and Friedel was subsequently extensively applied and further extended by J. D. H. Donnay (1940), and in many later papers by Donnay & Donnay, especially Donnay & Donnay (1974). The Viennese school of Tschermak (1904, 1906), Tschermak & Becke (1915), and Tertsch (1936) thoroughly analysed the morphology of twins, introduced the *Kantennormalengesetz* and established the minimal conditions for twinning. The structural and energy aspects of twins and their boundaries were first accentuated and developed by Buerger (1945). Presently, twinning plays an important (but negative) role in crystal structure determination. Several sophisticated computer programs have been developed that correct for the presence of twinning in a small single crystal.

A comprehensive review of twinning is given by Cahn (1954); an extensive treatment of mechanical twinning is presented in the monograph by Klassen-Neklyudova (1964). A tensor classification of twinning was recently presented by Wadhawan (1997, 2000). Brief modern surveys are contained in the textbooks by Bloss (1971), Giacomazzo (1992) and Indenbom (see Vainshtein *et al.*, 1995), the latter mainly devoted to theoretical aspects. In previous volumes of *International Tables*, two articles on twin-

ning have appeared: formulae for the calculation of characteristic twin data, based on the work by Friedel (1926, pp. 245–252), are collected by Donnay & Donnay in Section 3 of Volume II of the previous series (Donnay & Donnay, 1972), and a more mathematical survey is presented by Koch in Chapter 1.3 of Volume C of the present series (Koch, 2004).

Independently from the development of the concept of twinning in mineralogy and crystallography, summarized above, the concept of *domain structures* was developed in physics at the beginning of the 20th century. This started with the study of *ferromagnetism* by Weiss (1907), who put forward the idea of a molecular field and formulated the hypothesis of differently magnetized regions, called *ferromagnetic domains*, that can be switched by an external magnetic field. Much later, von Hámos & Thiessen (1931) succeeded in visualizing magnetic domains by means of colloidal magnetic powder. For more details about magnetic domains see Section 1.6.4 of the present volume.

In 1921, Valasek (1921) observed unusual dielectric behaviour in Rochelle salt and pointed out its similarity with anomalous properties of ferromagnetic materials. This analogy led to a prediction of ‘electric’ domains, *i.e.* regions with different directions of spontaneous polarization that can be switched by an electric field. Materials with this property were called *Seignette electrics* (derived from the French, ‘*sel de Seignette*’, denoting Rochelle salt). The term *seignettelectrics* is still used in Russian, but in English has been replaced by the term *ferroelectrics* (Mueller, 1935). Although many experimental and theoretical results gave indirect evidence for *ferroelectric domain structure* [for an early history see Cady (1946)], it was not until 1944 that Zwicker & Scherrer (1944) reported the first direct optical observation of the domain structure in ferroelectric potassium dihydrogen phosphate (KDP). Four years later, Klassen-Neklyudova *et al.* (1948) observed the domain structure of Rochelle salt in a polarizing microscope (see Klassen-Neklyudova, 1964, p. 27). In the same year, Blattner *et al.* (1948), Kay (1948) and Matthias & von Hippel (1948) visualized domains and domain walls in barium titanate crystals using the same technique.

These early studies also gave direct evidence of the influence of mechanical stress and electric field on domain structure. Further, it was disclosed that a domain structure exists only below a certain temperature, called the *Curie point*, and that the crystal structures below and above the Curie point have different point-group symmetries. The Curie point thus marks a structural phase transition between a *paraelectric phase* without a domain structure and a *ferroelectric phase* with a ferroelectric domain structure. Later, the term ‘Curie point’ was replaced by the more suitable expression *Curie temperature* or *transition temperature*.

The fundamental achievement in understanding phase transitions in crystals is the *Landau theory* of continuous phase transitions (Landau, 1937). Besides a thermodynamic explanation of anomalies near phase transitions, it discloses that any continuous phase transition is accompanied by a discontinuous decrease of crystal symmetry. In consequence, a phase with lower symmetry can always form a domain structure.

The basic role of symmetry was demonstrated in the pioneering work of Zheludev & Shuvalov (1956), who derived by simple crystallographic considerations the point groups of paraelectric and ferroelectric phases of all possible ferroelectric phase transitions and gave a formula for the number of ferroelectric domain states.

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