International Tables for Crystallography (2013). Vol. D, Section 3.4.1, pp. 484–486.

3.4. Domain structures

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3.4.1. Introduction

3.4.1.1. *Basic concepts*

It was demonstrated in Section 3.1.2 that a characteristic feature of structural phase transitions connected with a lowering of crystal symmetry is an anomalous behaviour near the transition, namely unusually large values of certain physical properties that vary strongly with temperature. In this chapter, we shall deal with another fundamental feature of structural phase transitions associated with symmetry lowering: the formation of a non-homogeneous, textured low-symmetry phase called a *domain structure*.

When a crystal homogeneous in the *parent* (prototypic, high-symmetry) phase undergoes a phase transition into a *ferroic* low-symmetry phase with lower point-group symmetry, then this ferroic phase is almost always formed as a non-homogeneous structure consisting of homogeneous regions called *domains* and contact regions between domains called *domain walls*. All domains have the same or the enantiomorphous crystal structure of the ferroic phase, but this structure has in different domains a different orientation, and sometimes also a different position in space. When a domain structure is observed by a measuring instrument, different domains can exhibit different tensor properties, different diffraction patterns and can differ in other physical properties. The domain structure can be visualized optically (see Fig. 3.4.1.1) or by other experimental techniques. Powerful high-resolution electron microscopy (HREM) techniques have made it possible to visualize atomic arrangements in domain structures (see Fig. 3.4.1.2). The appearance of a domain structure, detected by any reliable technique, provides the simplest unambiguous experimental proof of a structural phase transition.

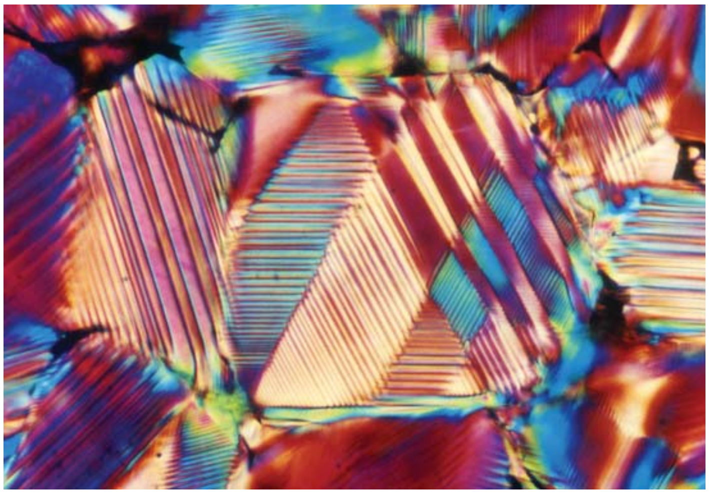

Fig. 3.4.1.1. Domain structure of tetragonal barium titanate ($BaTiO_3$). A thin section of barium titanate ceramic observed at room temperature in a polarized-light microscope (transmitted light, crossed polarizers). Courtesy of U. Täffner, Max-Planck-Institut für Metallforschung, Stuttgart. Different colours correspond to different ferroelastic domain states, connected areas of the same colour are ferroelastic domains and sharp boundaries between these areas are domain walls. Areas of continuously changing colour correspond to gradually changing thickness of wedge-shaped domains. An average distance between parallel ferroelastic domain walls is of the order of 1–10 µm.

Under the influence of external fields (mechanical stress, electric or magnetic fields, or combinations thereof), the domain structure can change; usually some domains grow while others decrease in size or eventually vanish. This process is called *domain switching*. After removing or decreasing the field a domain structure might not change considerably, *i.e.* the form of a domain pattern depends upon the field history: the domain structure exhibits *hysteresis* (see Fig. 3.4.1.3). In large enough fields, switching results in a reduction of the number of domains. Such a procedure is called *detwinning*. In rare cases, the crystal may consist of one domain only. Then we speak of a *single-domain crystal*.

There are two basic types of domain structures:

(i) Domain structures with one or several systems of parallel plane domain walls that can be observed in an optical or electron microscope. Two systems of perpendicular domain walls are often visible (see Fig. 3.4.1.4). In polarized light, domains exhibit different colours (see Fig. 3.4.1.1) and in diffraction experiments splitting of reflections can be observed (see Fig. 3.4.3.9). Domains can be switched by external mechanical stress. These features are typical for a *ferroelastic domain structure* in which neighbouring domains differ in mechanical strain (deformation). Ferroelastic domain structures can appear only in ferroelastic phases, *i.e.* as a result of a phase transition characterized by a decrease in the number of independent strain components (see Table 3.4.2.2).

(ii) Domain structures that are not visible using a polarized-light microscope and in whose diffraction patterns no splitting of reflections is observed. Special methods [*e.g.* etching, deposition of liquid crystals (see Fig. 3.4.1.5), electron or atomic force microscopy, or higher-rank optical effects (see Fig. 3.4.3.3)] are needed to visualize domains. Domains have the same strain and cannot usually be switched by an external mechanical stress. Such domain structures are called *non-ferroelastic domain structures*. They appear in all non-ferroelastic phases resulting from symmetry lowering that preserves the number of independent strain components (see Table 3.4.2.2).

Another important kind of domain structure is a *ferroelectric domain structure*, in which domains differ in the direction of the

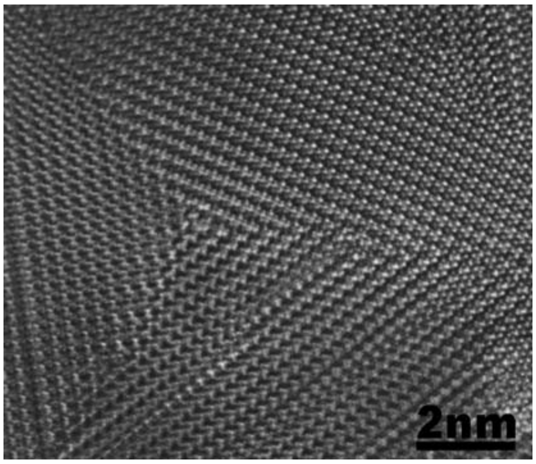

Fig. 3.4.1.2. Domain structure of a $BaGa_2O_4$ crystal seen by high-resolution transmission electron microscopy. Parallel rows are atomic layers. Different directions correspond to different ferroelastic domain states of domains, connected areas with parallel layers are different ferroelastic domains and boundaries between these areas are ferroelastic domain walls. Courtesy of H. Lemmens, EMAT, University of Antwerp.

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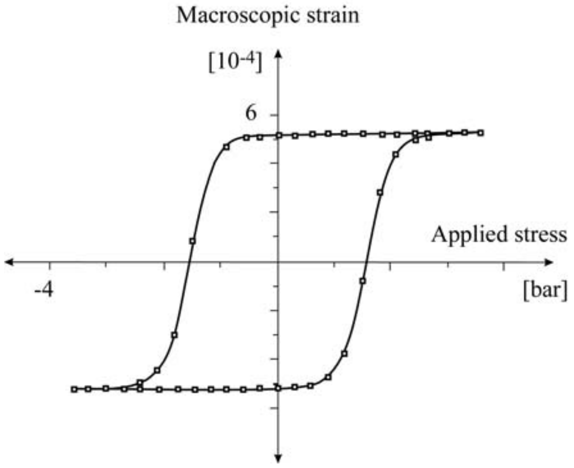

Fig. 3.4.1.3. Elastic hysteresis of ferroelastic lead phosphate $Pb_3(PO_4)_2$ (Salje, 1990). Courtesy of E. K. H. Salje, University of Cambridge. The dependence of strain on applied stress has the form of a loop. The states at the extreme left and right correspond to two ferroelastic domain states, steep parts of the loop represent switching of one state into the other by applied stress. The strain at zero stress corresponds to the last single-domain state formed in a field larger than the coercive stress defined by the stress at zero strain (the intersection of the loop with the axis of the applied stress). Similar dielectric hysteresis loops of polarization *versus* applied electric field are observed in ferroelectric phases (see *e.g.* Jona & Shirane, 1962).

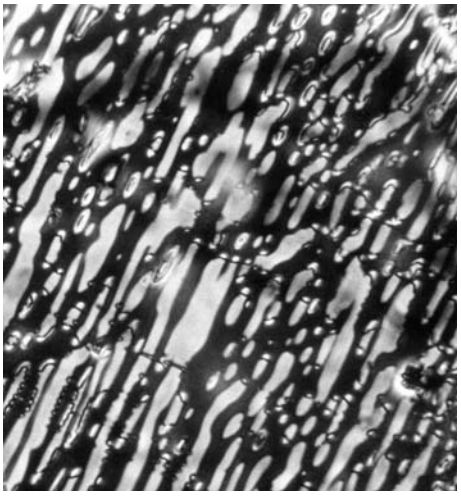

Fig. 3.4.1.5. Non-ferroelastic ferroelectric domains in triglycine sulfate (TGS) revealed by a liquid-crystal method. A thin layer of a nematic liquid crystal deposited on a crystal surface perpendicular to the spontaneous polarization is observed in a polarized-light microscope. Black and white areas correspond to ferroelectric domains with antiparallel spontaneous polarization. The typical size of the domains is of order of 1–10μm. Courtesy of M. Połomska, Institute of Molecular Physics, PAN, Poznań. Although one preferential direction of domain walls prevails, the rounded shapes of the domains indicate that all orientations of non-ferroelastic walls are possible.

spontaneous polarization. Such a domain structure is formed at ferroelectric phase transitions that are characterized by the appearance of a new polar direction in the ferroic phase. Ferroelectric domains can usually be switched by external electric fields. Two ferroelectric domains with different directions of spontaneous polarization can have different spontaneous strain [*e.g.* in dihydrogen phosphate (KDP) crystals, two ferroelectric domains with opposite directions of the spontaneous polarization have different spontaneous shear strain], or two ferroelectric domains with antiparallel spontaneous polarization can possess the same strain [*e.g.* in triglycine sulfate (TGS) crystals].

The physical properties of polydomain crystals are significantly influenced by their domain structure. The values of important material property tensor components, *e.g.* permittivity, piezoelectric and elastic coefficients, may be enhanced or diminished by the presence of a domain structure. Owing to switching and detwinning phenomena, polydomain materials exhibit hysteresis of material properties. These features have important practical implications, *e.g.* the production of anisotropic ceramic materials or ferroelectric memories.

Fig. 3.4.1.4. Transmission electron microscopy image of the ferroelastic domain structure in a $YBa_2Cu_3O_{7-y}$ crystal (Rosová, 1999). Courtesy of A. Rosová, Institute of Electrical Engineering, SAS, Bratislava. There are two systems ('complexes'), each of which is formed by almost parallel ferroelastic domain walls with needle-like tips. The domain walls in one complex are nearly perpendicular to the domain walls in the other complex.

The domain structure resulting from a structural phase transition belongs to a special type of twinning referred to as *transformation twinning* (see Section 3.3.7.2). Despite this, the current terminology used in domain-structure studies is different. The main terms were coined during the first investigations of ferroelectric materials, where striking similarities with the behaviour of ferromagnetic materials led researchers to introduce terms analogous to those used in studies of ferromagnetic domain structures that had been examined well at that time.

Bicrystallography (see Section 3.2.2) provides another possible frame for discussing domain structures. Bicrystallography and domain-structure analysis have developed independently and almost simultaneously but different language has again precluded deeper confrontation. Nevertheless, there are common features in the methodology of both approaches, in particular, the principle of symmetry compensation (see Section 3.2.2), which plays a fundamental role in both theories.

In Chapter 3.1, it is shown that the anomalous behaviour near phase transitions can be explained in the framework of the Landau theory. In this theory, the formation of the domain structures follows from the existence of several equivalent solutions for the order parameter. This result is a direct consequence of a symmetry reduction at a ferroic phase transition. It is this dissymmetrization which is the genuine origin of the domain-structure formation and which determines the basic static features of all domain structures.

3.4.1.2. *Scope of this chapter*

This chapter is devoted to the crystallographic aspects of static domain structures, especially to the symmetry analysis of these structures. The main aim is to explain basic concepts, derive relations that govern the formation of domain structures and provide tables with useful ready-to-use data on domain structures of ferroic phases. The exposition uses algebraic tools that are explained in Section 3.2.3, but the important points are illustrated with simple examples comprehensible even without mathematical details. The synoptic tables in Sections 3.4.2 and 3.4.3 present the main results of the analysis for all possible ferroic domain structures. More detailed information on certain points can be found in the software *GI⋆KoBo*-1.

All these results are definite – their validity does not depend on any particular model or approximation – and form thus a firm basis for further more detailed quantitative treatments. '*For the most part, the only exact statements which can be made about a solid state system are those which arise as a direct consequence of symmetry alone.*' (Knox & Gold, 1967.)

The exposition starts with domain states, continues with pairs of domain states and domain distinction, and terminates with domain twins and walls. This is also the sequence of steps in domain-structure analysis, which proceeds from the simplest to more complicated objects.

In Section 3.4.2, we explain the concept of *domain states* (also called variants or orientational states), define different types of domain states (principal, ferroelastic, ferroelectric, basic), find simple formulae for their number, and disclose their hierarchy and relation with symmetry lowering and with order parameters of the transition. Particular results for all possible ferroic phase transitions can be found in synoptic Table 3.4.2.7, which lists all possible crystallographically non-equivalent *point-group symmetry descents that may appear at a ferroic phase transition*. For each descent, all independent twinning groups (characterizing the relation between two domain states) are given together with the number of principal, ferroelastic and ferroelectric domain states and other data needed in further analysis.

Section 3.4.3 deals with *pairs of domain states* and with the relationship between two domain states in a pair. This relationship, in mineralogy called a 'twin law', determines the distinction between domain states, specifies switching processes between two domain states and forms a starting point for discussing domain walls and twins. We show different ways of expressing the relation between two domain states of a domain pair, derive a classification of domain pairs, find non-equivalent domain pairs and determine which tensor properties are different and which are the same in two domain states of a domain pair.

The presentation of non-equivalent domain pairs is divided into two parts. Synoptic Table 3.4.3.4 lists all representative *non-equivalent non-ferroelastic domain pairs*, and for each pair gives the twinning groups, and the number of tensor components that are different and that are the same in two domain states. These numbers are given for all important property tensors up to rank four. We also show how these data can be used to determine switching forces between two non-ferroelastic domain states.

Then we explain specific features of ferroelastic domain pairs: compatible (permissible) domain walls and disorientation of domain states in ferroelastic domain twins. A list of all non-equivalent ferroelastic domain pairs is presented in two tables. Synoptic Table 3.4.3.6 contains all *non-equivalent ferroelastic domain pairs with compatible (coherent) domain walls*. This table gives the orientation of compatible walls and their symmetry properties. Table 3.4.3.7 lists all *non-equivalent ferroelastic domain pairs with no compatible ferroelastic domain walls*.

Column K_{1j} in Table 3.4.2.7 specifies all representative non-equivalent domain pairs that can appear in each particular phase transition; in combination with Tables 3.4.3.4 and 3.4.3.6, it allows one to determine the main features of any ferroic domain structure.

Section 3.4.4 is devoted to domain twins and domain walls. We demonstrate that the symmetry of domain twins and domain walls is described by layer groups, give a classification of domain twins and walls based on their symmetry, and present possible layer groups of non-ferroelastic and ferroelastic domain twins and walls. Then we discuss the properties of finite-thickness domain walls. In an example, we illustrate the symmetry analysis of microscopic domain walls and present conclusions that can be drawn from this analysis about the microscopic structure of domain walls.

The exposition is given in the continuum description with crystallographic point groups and property tensors. In this approach, all possible cases are often treatable and where possible are covered in synoptic tables or – in a more detailed form – in the software *GI⋆KoBo*-1. Although the group-theoretical tools are almost readily transferable to the microscopic description (using the space groups and atomic positions), the treatment of an inexhaustible variety of microscopic situations can only be illustrated by particular examples.

Our attempt to work with well defined notions calls for introducing several new, and generalizing some accepted, concepts. Also an extended notation for the symmetry operations and groups has turned out to be indispensable. Since there is no generally accepted terminology on domain structures yet, we often have to choose a term from several existing more-or-less equivalent variants.

The specialized scope of this chapter does not cover many other important aspects of domain-structure studies. More information can be found in the following references. The only comprehensive monograph, by Tagancev *et al.* (2010), provides a thorough treatise on major topics of domain structure in non-magnetic ferroic crystals and thin films. There are two specialized monographs: the booklet by Fesenko *et al.* (1990) deals with experimental aspects of domain structure in multi-axial ferroelectrics and Sidorkin (2002, 2006) concentrates on the theoretical treatment of phenomenological models of various problems of domain-structure studies. The main concepts of domain structures of ferroic materials are explained in the book by Wadhawan (2000) and in a review by Schranz (1995). Ferroelastic domain structures are reviewed in Boulesteix (1984) and Wadhawan (1991), and are treated in detail by Salje (1990, 1991, 2000*a*,*b*). The main properties of ferroelectric domain structures are explained in older books or reviews on ferroelectric crystals: Känzig (1957), Jona & Shirane (1962), Fatuzzo & Merz (1967), Mitsui *et al.* (1976), Lines & Glass (1977), Smolenskii *et al.* (1984), Zheludev (1988) and Strukov & Levanyuk (1998). Recent books and reviews on ferroic materials rarely contain new, informed and unifying views on admirable experimental achievements in this field. Applications of ferroelectrics are also described in now older books by Xu (1991) and Uchino (2000). Principles and technical aspects of ferroelectric memories were reviewed by Scott (1998, 2000).

3.4.2. Domain states

3.4.2.1. *Principal and basic domain states*

As for all crystalline materials, domain structures can be approached in two ways: In the *microscopic description*, a crystal is treated as a regular arrangement of atoms. Domains differ in tiny differences of atomic positions which can be determined only indirectly, *e.g.* by diffraction techniques. In what follows, we shall pay main attention to the *continuum description*, in which a crystal is treated as an anisotropic continuum. Then the crystal properties are described by property tensors (see Section 1.1.1) and the crystal symmetry is expressed by crystallographic point groups. In this approach, domains exhibit different tensor properties that enable one to visualize domains by optical or other methods.

The domain structure observed in a microscope appears to be a patchwork of homogeneous regions – domains – that have various colours and shapes (see Fig. 3.4.1.1). Indeed, the usual description considers a domain structure as a collection of domains and contact regions of domains called domain walls. Strictly speaking, by a *domain* $\mathbf{D}_i$ one understands a connected part of the crystal, called the *domain region*, which is filled with a

references