3.4. DOMAIN STRUCTURES

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 several important aspects of domain structures. More information can be found in the following references. There are only two monographs on domain structures (both in Russian): Fesenko *et al.* (1990) and Sidorkin (2002). 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, 2000a,b). Different aspects of ferroelectric domain structures are covered in 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). Applications of ferroelectrics are described in the books by Xu (1991) and Uchino (2000). Principles and technical aspects of ferroelectric memories are 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 homogeneous low-symmetry crystal structure. *Domain walls* can be associated with the boundaries of domain regions. The interior homogeneous bulk structure within a domain region will be called a *domain state*. Equivalent terms are *variant* or *structural variant* (Van Tendeloo & Amelinckx, 1974). We shall use different adjectives to specify domain states. In the microscopic description, domain states associated with the primary order parameter will be referred to as *primary* (*microscopic*, *basic*) *domain states*. In the macroscopic description, the primary domain states will be called *principal domain states*, which correspond to Aizu's *orientation states*. (An exact definition of principal domain states is given below.)
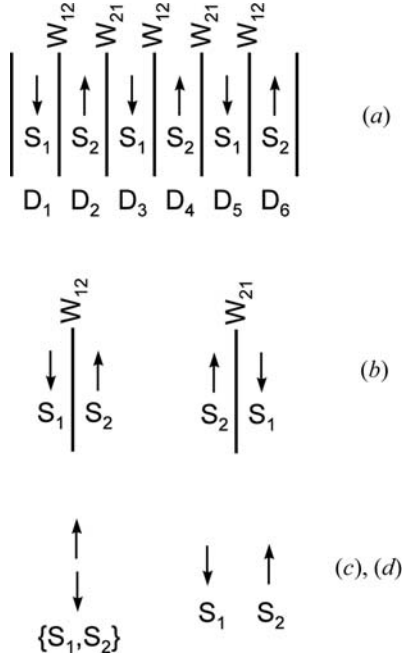
Fig. 3.4.2.1. Hierarchy in domain-structure analysis. (*a*) Domain structure consisting of domains $\mathbf{D}_1, \mathbf{D}_2, \ldots, \mathbf{D}_6$ and domain walls $\mathbf{W}_{12}$ and $\mathbf{W}_{21}$; (*b*) domain twin and reversed twin (with reversed order of domain states); (*c*) domain pair consisting of two domain states $\mathbf{S}_1$ and $\mathbf{S}_2$; (*d*) domain states $\mathbf{S}_1$ and $\mathbf{S}_2$.

Further useful division of domain states is possible (though not generally accepted): Domain states that are specified by a constant value of the spontaneous strain are called *ferroelastic domain states*; similarly, *ferroelectric domain states* exhibit constant spontaneous polarization *etc*. Domain states that differ in some tensor properties are called *ferroic* or *tensorial domain states etc.* If no specification is given, the statements will apply to any of these domain states.

A domain $\mathbf{D}_i$ is specified by a domain state $\mathbf{S}_j$ and by domain region B_k: $\mathbf{D}_i = \mathbf{D}_i(\mathbf{S}_j, B_k)$. Different domains may possess the same domain state but always differ in the domain region that specifies their shape and position in space.

The term 'domain' has also often been used for a domain state. Clear distinction of these two notions is essential in further considerations and is illustrated in Fig. 3.4.2.1. A ferroelectric domain structure (Fig. 3.4.2.1*a*) consists of six ferroelectric domains $\mathbf{D}_1, \mathbf{D}_2, \ldots, \mathbf{D}_6$ but contains only two domain states $\mathbf{S}_1, \mathbf{S}_2$ characterized by opposite directions of the spontaneous polarization depicted in Fig. 3.4.2.1(*d*). Neighbouring domains have different domain states but non-neighbouring domains may possess the same domain state. Thus domains with odd serial number have the domain state $\mathbf{S}_1$ (spontaneous polarization 'down'), whereas domains with even number have domain state $\mathbf{S}_2$ (spontaneous polarization 'up').

A great diversity of observed domain structures are connected mainly with various dimensions and shapes of domain regions, whose shapes depend sensitively on many factors (kinetics of the phase transition, local stresses, defects *etc.*). It is, therefore, usually very difficult to interpret in detail a particular observed domain pattern. Domain states of domains are, on the other hand, governed by simple laws, as we shall now demonstrate.

We shall consider a ferroic phase transition with a symmetry lowering from a parent (prototypic, high-symmetry) phase with symmetry described by a point group G to a ferroic phase with the point-group symmetry F_1, which is a subgroup of G. We shall denote this dissymmetrization by a group–subgroup symbol $G \supset F_1$ (or $G \Downarrow F_1$ in Section 3.1.3) and call it a *symmetry descent* or *dissymmetrization*. Aizu (1970*a*) calls these symmetry descents *species* and uses the letter F instead of the symbol $\subset$.
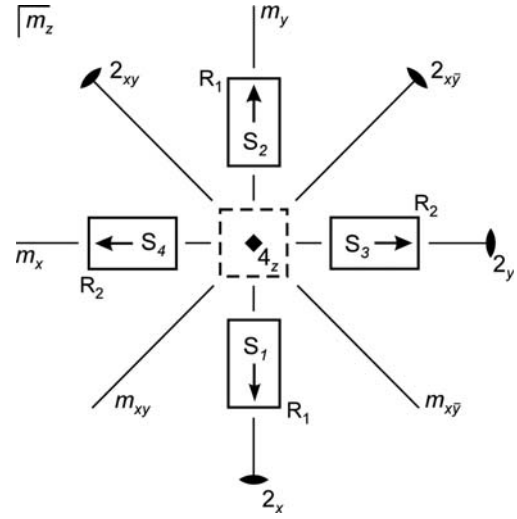

Fig. 3.4.2.2. Exploded view of single-domain states $\mathbf{S}_1$, $\mathbf{S}_2$, $\mathbf{S}_3$ and $\mathbf{S}_4$ (solid rectangles with arrows of spontaneous polarization) formed at a phase transition from a parent phase with symmetry $G = 4_z/m_z m_x m_{xy}$ to a ferroic phase with symmetry $F_1 = 2_x m_y m_z$. The parent phase is represented by a dashed square in the centre with the symmetry elements of the parent group $G = 4_z/m_z m_x m_{xy}$ shown.

As an illustrative example, we choose a phase transition with parent symmetry $G = 4_z/m_z m_x m_{xy}$ and ferroic symmetry $F_1 = 2_x m_y m_z$ (see Fig. 3.4.2.2). Strontium bismuth tantalate (SBT) crystals, for instance, exhibit a phase transition with this symmetry descent (Chen *et al.*, 2000). Symmetry elements in the symbols of G and F_1 are supplied with subscripts specifying the orientation of the symmetry elements with respect to the reference coordinate system. The necessity of this extended notation is exemplified by the fact that the group $G = 4_z/m_z m_x m_{xy}$ has six subgroups with the same 'non-oriented' symbol $mm2$: $m_x m_y 2_z$, $2_x m_y m_z$, $m_x 2_y m_z$, $m_{x\bar{y}} m_{xy} 2_z$, $2_{x\bar{y}} m_{xy} m_z$, $m_{x\bar{y}} 2_{xy} m_z$. Lower indices thus specify these subgroups unequivocally and the example illustrates an important rule of domain-structure analysis: *All symmetry operations, groups and tensor components must be related to a common reference coordinate system and their orientation in space must be clearly specified.*

The physical properties of crystals in the continuum description are expressed by property tensors. As explained in Section 1.1.4, the crystal symmetry reduces the number of independent components of these tensors. Consequently, for each property tensor the number of independent components in the low-symmetry ferroic phase is the same or higher than in the high-symmetry parent phase. Those tensor components or their linear combinations that are zero in the high-symmetry phase and nonzero in the low-symmetry phase are called *morphic tensor components* or *tensor parameters* and the quantities that appear only in the low-symmetry phase are called *spontaneous quantities* (see Section 3.1.3.2). The morphic tensor components and spontaneous quantities thus reveal the difference between the high- and low-symmetry phases. In our example, the symmetry $F_1 = 2_x m_y m_z$ allows a nonzero spontaneous polarization $\mathbf{P}_0^{(f)} = (P, 0, 0)$, which must be zero in the high-symmetry phase with $G = 4_z/m_z m_x m_{xy}$.

We shall now demonstrate in our example that the symmetry lowering at the phase transition leads to the existence of several equivalent variants (domain states) of the low-symmetry phase. In Fig. 3.4.2.2, the parent high-symmetry phase is represented in the middle by a dashed square that is a projection of a square prism with symmetry $4_z/m_z m_x m_{xy}$. A possible variant of the low-symmetry phase can be represented by an oblong prism with a vector representing the spontaneous polarization. In Fig. 3.4.2.2, the projection of this oblong prism is drawn as a rectangle which is shifted out of the centre for better recognition. We denote by $\mathbf{S}_1$ a homogeneous low-symmetry phase with spontaneous polar-

ization $P_0^{(1)} = (P, 0, 0)$ and with symmetry $F_1 = 2_x m_y m_z$. Let us, mentally, increase the temperature to above the transition temperature and then apply to the high-symmetry phase an operation 2_z, which is a symmetry operation of this high-symmetry phase but not of the low-symmetry phase. Then decrease the temperature to below the transition temperature. The appearance of another variant of the low-symmetry phase S_2 with spontaneous polarization $P_0^{(2)} = (-P, 0, 0)$ obviously has the same probability of appearing as had the variant S_1. Thus the two variants of the low-symmetry phase S_1 and S_2 can appear with the same probability if they are related by a symmetry operation suppressed (lost) at the transition, *i.e.* an operation that was a symmetry operation of the high-symmetry phase but is not a symmetry operation of the low-symmetry phase S_1. In the same way, the lost symmetry operations 4_z and 4_z^3 generate from S_1 two other variants, S_3 and S_4, with spontaneous polarizations $(0, P, 0)$ and $(0, -P, 0)$, respectively. Variants of the low-symmetry phase that are related by an operation of the high-symmetry group G are called *crystallographically equivalent (in G) variants*. Thus we conclude that *crystallographically equivalent (in G) variants of the low-symmetry phase have the same chance of appearing*.

We shall now make similar considerations for a general ferroic phase transition with a symmetry descent $G \supset F_1$. By the *state* S *of a crystal* we shall understand, in the continuum description, the set of all its properties expressed by property (matter) tensors in the reference Cartesian crystallophysical coordinate system of the parent phase (see Example 3.2.3.9 in Section 3.2.3.3.1). A state defined in this way may change not only with temperature and external fields but also with the orientation of the crystal in space.

We denote by S_1 a state of a homogeneous ferroic phase. If we apply to S_1 a symmetry operation g_i of the group G, then the ferroic phase in a new orientation will have the state S_j, which may be identical with S_1 or different. Using the concept of group action (explained in detail in Section 3.2.3.3.1) we express this operation by a simple relation:

$$g_j S_1 = S_j, \quad g_j \in G. \qquad (3.4.2.1)$$

Let us first turn our attention to operations $f_j \in G$ that do not change the state S_1:

$$f_j S_1 = S_j, \quad f_j \in G. \qquad (3.4.2.2)$$

The set of all operations of G that leave S_1 invariant form a group called a *stabilizer* (or *isotropy group*) of a state S_1 in the group G. This stabilizer, denoted by $I_G(S_1)$, can be expressed explicitly in the following way:

$$I_G(S_1) \equiv \{g \in G | g S_1 = S_1\}, \qquad (3.4.2.3)$$

where the right-hand part of the equation should be read as 'a set of all operations of G that do not change the state S_1' (see Section 3.2.3.3.2).

Here we have to explain the difference between the concept of a stabilizer of an object and the symmetry of that object. By the *symmetry group F of an object* one understands the set of all operations (isometries) that leave this object S invariant. The symmetry group F of an object is considered to be an inherent property that does not depend on the orientation and position of the object in space. (The term *eigensymmetry* is used in Chapter 3.3 for symmetry groups defined in this way.) In this case, the symmetry elements of F are 'attached' to the object.

A stabilizer describes the symmetry properties of an object in another way, in which the object and the group of isometries are decoupled. One is given a group G, the symmetry elements of which have a defined orientation in a fixed reference system. The object can have any orientation in this reference system. Those operations of G that map the object in a given orientation onto itself form the *stabilizer $I_G(S_1)$ of S_i in the group G*. In this case,

the stabilizer depends on the orientation of the object in space and is expressed by an 'oriented' group symbol F_1 with subscripts defining the orientation of the symmetry elements of F_1. Only for certain 'prominent' orientations will the stabilizer acquire a symmetry group of the same crystal class (crystallographic point group) as the *eigensymmetry* of the object.

We shall define a *single-domain orientation* as a prominent orientation of the crystal in which the stabilizer $I_G(S_1)$ of its state S_1 is equal to the symmetry group F_1 which is, after removing subscripts specifying the orientation, identical with the *eigensymmetry* of the ferroic phase:

$$I_G(S_1) = F_1. \qquad (3.4.2.4)$$

This equation thus declares that the crystal in the state S_1 has a prominent single-domain orientation.

The concept of the stabilizer allows us to identify the '*eigensymmetry*' of a domain state (or an object in general) S_i with the crystallographic class (non-oriented point group) of the stabilizer of this state in the group of all rotations $O(3)$, $I_{O(3)}(S_i)$.

Since we shall further deal mainly with states of the ferroic phase in single-domain orientations, we shall use the term 'state' for a 'state of the crystal in a single-domain orientation', unless mentioned otherwise. Then the stabilizer $I_G(S_1)$ will often be replaced by the group F_1, although all statements have been derived and hold for stabilizers.

The difference between symmetry groups of a crystal and stabilizers will become more obvious in the treatment of secondary domain states in Section 3.4.2.2 and in discussing disoriented ferroelastic domain states (see Section 3.4.3.6.3).

As we have seen in our illustrative example, the suppressed operations generate from the first state S_1 other states. Let g_j be such a *suppressed operation*, *i.e.* $g_j \in G$ but $g_j \notin F_1$. Since all operations that retain S_1 are collected in F_1, the operation g_j must transform S_1 into another state S_j,

$$g_j S_1 = S_j \neq S_1, \quad g_j \in G, \quad g_j \notin F_1, \qquad (3.4.2.5)$$

and we say that the state S_j is *crystallographically equivalent (in G) with* the state S_1, $S_j \overset{G}{\sim} S_1$.

We define *principal domain states* as crystallographically equivalent (in G) variants of the low-symmetry phase in single-domain orientations that can appear with the same probability in the ferroic phase. They represent possible macroscopic bulk structures of (1) ferroic single-domain crystals, (2) ferroic domains in non-ferroelastic domain structures (see Section 3.4.3.5), or (3) ferroic domains in any ferroic domain structure, if all spontaneous strains are suppressed [this is the so-called parent clamping approximation (PCA), see Section 3.4.2.5]. In what follows, *any statement formulated for principal domain states or for single-domain states applies to any of these three situations*. Principal domain states are identical with *orientation states* (Aizu, 1969) or *orientation variants* (Van Tendeloo & Amelinckx, 1974). The adjective 'principal' distinguishes these domain states from primary (microscopic, basic – see Section 3.4.2.5) domain states and secondary domain states, defined in Section 3.4.2.2, and implies that any two of these domain states differ in principal tensor parameters (these are linear combinations of morphic tensor components that transform as the primary order parameter of an equitranslational phase transition with a point-group symmetry descent $G \supset F_1$, see Sections 3.1.3.2 and 3.4.2.3). A simple criterion for a principal domain state S_1 is that its stabilizer in G is equal to the symmetry F_1 of the ferroic phase [see equation (3.4.2.4)].

When one applies to a principal domain state S_1 all operations of the group G, one gets all principal domain states that are crystallographically equivalent with S_1. The set of all these states is denoted GS_1 and is called an *G-orbit of* S_1 (see also Section 3.2.3.3.3),

$$GS_1 = \{S_1, S_2, \ldots, S_n\}. \qquad (3.4.2.6)$$

In our example, the G-orbit is $4_z/m_zm_xm_{xy}S_1 = \{S_1, S_2, S_3, S_4\}$.

Note that any operation g from the parent group G leaves the orbit GS_1 invariant since its action results only in a permutation of all principal domain states. This change does not alter the orbit, since the orbit is a set in which the sequence (order) of objects is irrelevant. Therefore, the *orbit GS_1 is invariant under the action of the parent group G*, $GGS_1 = GS_1$.

A ferroic phase transition is thus a paradigmatic example of the law of symmetry compensation (see Section 3.2.2): The dissymmetrization of a high-symmetry parent phase into a low-symmetry ferroic phase produces variants of the low-symmetry ferroic phase (single-domain states). Any two single-domain states are related by some suppressed operations of the parent symmetry that are missing in the ferroic symmetry and the set of all single-domain states (G-orbit of domain states) recovers the symmetry of the parent phase. If the domain structure contains all domain states with equal partial volumes then the average symmetry of this polydomain structure is, in the first approximation, identical to the symmetry of the parent phase.

Now we find a simple formula for the number n of principal domain states in the orbit GS_1 and a recipe for an efficient generation of all principal domain states in this orbit.

The fact that all operations of the group $I_G(S_1) = F_1$ leave S_1 invariant can be expressed in an abbreviated form in the following way [see equation (3.2.3.70)]:

$$F_1 S_1 = S_1. \qquad (3.4.2.7)$$

We shall use this relation to derive all operations that transform S_1 into $S_j = g_jS_1$:

$$g_jS_1 = g_j(F_1S_1) = (g_jF_1)S_1 = S_j, \quad g_j \in G. \qquad (3.4.2.8)$$

The second part of equation (3.4.2.8) shows that all lost operations that transform S_1 into S_j are contained in the left coset g_jF_1 (for left cosets see Section 3.2.3.2.3).

It is shown in group theory that two left cosets have no operation in common. Therefore, another left coset g_kF_1 generates another principal domain state S_k that is different from principal domain states S_1 and S_j. Equation (3.4.2.8) defines, therefore, a one-to-one relation between principal domain states of the orbit GS_1 and left cosets of F_1 [see equation (3.2.3.69)],

$$S_j \leftrightarrow g_jF_1, \quad F_1 = I_G(S_1), \quad j = 1, 2, \ldots, n. \qquad (3.4.2.9)$$

From this relation follow two conclusions:

(1) The number n of principal domain states equals the number of left cosets of F_1. All different left cosets of F_1 constitute the decomposition of the group G into left cosets of F_1 [see equation (3.2.3.19)],

$$G = g_1F_1 \cup g_2F_1 \cup \ldots \cup g_jF_1 \cup \ldots \cup g_nF_1, \qquad (3.4.2.10)$$

where the symbol $\cup$ is a union of sets and the number n of left cosets is called the *index of G in F_1* and is denoted by the symbol $[G : F_1]$. Usually, one chooses for g_1 the identity operation e; then the first left coset equals F_1. Since each left coset contains $|F_1|$ operations, where $|F_1|$ is number of operations of F_1 (order of F_1), the number of left cosets in the decomposition (3.4.2.10) is

$$n = [G : F_1] = |G| : |F_1|, \qquad (3.4.2.11)$$

where $|G|$, $|F_1|$ are orders of the point groups G, F_1, respectively. The index n is a quantitative measure of the degree of dissymmetrization $G \supset F_1$. Thus *the number of principal domain states in orbit GS_1 is equal to the index of F_1 in G, i.e. to the number of operations of the high-symmetry group G divided by the number of operations of the low-symmetry phase F_1*. In our illustrative example we get $n = |4_z/m_zm_xm_{xy}| : |2_xm_ym_z| = 16 : 4 = 4$.

The basic formula (3.4.2.11) expresses a remarkable result: the number n of principal domain states is determined by how many times the number of symmetry operations increases at the transition from the low-symmetry group F_1 to the high-symmetry group G, or, the other way around, the fraction $\frac{1}{n}$ is a quantitative measure of the symmetry decrease from G to F_1, $|F_1| = \frac{1}{n}|G|$. Thus *it is not the concrete structural change, nor even the particular symmetries of both phases, but only the extent of dissymmetrization that determines the number of principal domain states*. This conclusion illustrates the fundamental role of symmetry in domain structures.

(2) Relation (3.4.2.9) yields a *recipe for calculating all principal domain states of the orbit GS_1*: One applies successively to the first principal domain states S_1 the representatives of all left cosets of F_1:

$$GS_1 = \{S_1, g_2S_1, \ldots, g_jS_1, \ldots, g_nS_1\}, \qquad (3.4.2.12)$$

where the operations $g_1 = e, g_2, \ldots, g_j, \ldots, g_n$ are the representatives of left cosets in the decomposition (3.4.2.10) and e is an identity operation. We add that any operation of a left coset can be chosen as its representative, hence the operation g_j can be chosen arbitrarily from the left coset g_jF_1, $j = 1, 2, \ldots, n$.

This result can be illustrated in our example. Table 3.4.2.1 presents in the first column the four left cosets $g_j\{2_xm_ym_z\}$ of the group $F_1 = 2_xm_ym_z$. The corresponding principal domain states S_j, $j = 1, 2, 3, 4$, and the values of spontaneous polarization in these principal domain states are given in the second and the third columns, respectively. It is easy to verify in Fig. 3.4.2.2 that all operations of each left coset transform the first principal domain state S_1 into one principal domain state S_j, $j = 2, 3, 4$.

The left coset decompositions of all crystallographic point groups and their subgroup symmetry are available in the software *GI$\star$KoBo*-1, path: *Subgroups\View\Twinning Group*.

Let us turn briefly to the symmetries of the principal domain states. From Fig. 3.4.2.2 we deduce that two domain states S_1 and S_2 in our illustrative example have the same symmetry, $F_1 = F_2 = 2_xm_ym_z$, whereas two others S_3 and S_4 have another symmetry, $F_3 = F_4 = m_x2_ym_z$. We see that symmetry does not specify the principal domain state in a unique way, although a principal domain state S_j has a unique symmetry $F_i = I_G(S_j)$.

It turns out that if g_j transforms S_1 into S_j, then the symmetry group F_j of S_j is conjugate by g_j to the symmetry group F_1 of S_1 [see Section 3.2.3.3, Proposition 3.2.3.13 and equation (3.2.3.55)]:

$$\text{if } S_j = g_jS_1, \text{ then } F_j = g_jF_1g_j^{-1}. \qquad (3.4.2.13)$$

One can easily check that in our example each operation of the second left coset of $F_1 = 2_xm_ym_z$ (second row in Table 3.4.2.1) transforms $F_1 = 2_xm_ym_z$ into itself, whereas operations from the

Table 3.4.2.1. *Left and double cosets, principal and secondary domain states and their tensor parameters for the phase transition with* $G = 4_z/m_zm_xm_{xy}$ *and* $F_1 = 2_xm_ym_z$

Left cosets g_jS_1				Principal domain states			Secondary domain states		
1	2_x	m_y	m_z	S_1	$(P00)$	$(000g00)$	R_1	$u_1 - u_2$	$Q_{11} - Q_{22}$
$\bar{1}$	m_x	2_y	2_z	S_2	$(-P00)$	$(000-g00)$			
2_{xy}	4_z	$\bar{4}_z^3$	$m_{x\bar{y}}$	S_3	$(0P0)$	$(0000-g0)$	R_2	$u_2 - u_1$	$Q_{22} - Q_{11}$
$2_{x\bar{y}}$	4_z^3	$\bar{4}_z$	m_{xy}	S_4	$(0-P0)$	$(0000g0)$			

third and fourth left cosets yield $F_3 = F_4 = m_x 2_y m_z$. We shall return to this issue again at the end of Section 3.4.2.2.3.

3.4.2.2. *Secondary domain states, partition of domain states*

In this section we demonstrate that any morphic (spontaneous) property appears in the low-symmetry phase in several equivalent variants and find what determines their number and basic properties.

As we saw in Fig. 3.4.2.2, the spontaneous polarization – a principal tensor parameter of the $4_z/m_z m_x m_{xy} \supset 2_x m_y m_z$ phase transition – can appear in four different directions that define four principal domain states. Another morphic property is a spontaneous strain describing the change of unit-cell shape; it is depicted in Fig. 3.4.2.2 as a transformation of a square into a rectangle. This change can be expressed by a difference between two strain components $u_{11} - u_{22} = \lambda^{(1)}$, which is a morphic tensor parameter since it is zero in the parent phase and nonzero in the ferroic phase. The quantity $\lambda^{(1)} = u_{11} - u_{22}$ is a secondary order parameter of the transition $4_z/m_z m_x m_{xy} \supset 2_x m_y m_z$ (for secondary order parameters see Section 3.1.3.2).

From Fig. 3.4.2.2, we see that two domain states $\mathbf{S}_1$ and $\mathbf{S}_2$ have the same spontaneous strain, whereas $\mathbf{S}_3$ and $\mathbf{S}_4$ exhibit another spontaneous strain $\lambda^{(2)} = u_{22} - u_{11} = -\lambda^{(1)}$. Thus we can infer that a property 'to have the same value of spontaneous strain' divides the four principal domain states $\mathbf{S}_1$, $\mathbf{S}_2$, $\mathbf{S}_3$ and $\mathbf{S}_4$ into two classes: $\mathbf{S}_1$ and $\mathbf{S}_2$ with the same spontaneous strain $\lambda^{(1)}$ and $\mathbf{S}_3$ and $\mathbf{S}_4$ with the same spontaneous strain $\lambda^{(2)} = -\lambda^{(1)}$. Spontaneous strain appears in two 'variants': $\lambda^{(1)}$ and $\lambda^{(2)} = -\lambda^{(1)}$.

We can define a *ferroelastic domain state* as a state of the crystal with a certain value of spontaneous strain λ, irrespective of the value of the principal order parameter. Values $\lambda = \lambda^{(1)}$ and $\lambda^{(2)} = -\lambda^{(1)}$ thus specify two ferroelastic domain states $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively. The spontaneous strain in this example is a secondary order parameter and the ferroelastic domain states can therefore be called *secondary domain states*.

An algebraic version of the above consideration can be deduced from Table 3.4.2.1, where to each principal domain state (given in the second column) there corresponds a left coset of $F_1 = 2_x m_y m_z$ (presented in the first column). Thus to the partition of principal domain states into two subsets

$$\{\mathbf{S}_1, \mathbf{S}_2, \mathbf{S}_3, \mathbf{S}_4\} = \{\mathbf{S}_1, \mathbf{S}_2\}_{\lambda^{(1)}} \cup \{\mathbf{S}_3, \mathbf{S}_4\}_{\lambda^{(2)}}, \quad (3.4.2.14)$$

there corresponds, according to relation (3.4.2.9), a partition of left cosets

$$
\begin{aligned}
4_z/&m_z m_x m_{xy} \\
&= \{\{2_x m_y m_z\} \cup \bar{1}\{2_x m_y m_z\}\} \cup \{2_{xy}\{2_x m_y m_z\} \cup 2_{xy}\{2_x m_y m_z\}\} \\
&= m_x m_y m_z \cup 2_{xy}\{m_x m_y m_z\}, \quad (3.4.2.15)
\end{aligned}
$$

where we use the fact that the union of the first two left cosets of $2_x m_y m_z$ is equal to the group $m_x m_y m_z$. This group is the stabilizer of the first ferroelastic domain state $\mathbf{R}_1$, $I_G(\mathbf{R}_1) = m_x m_y m_z$. Two left cosets of $m_x m_y m_z$ correspond to two ferroelastic domain states, $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively. Therefore, the number n_a of ferroelastic domain states is equal to the number of left cosets of $m_x m_y m_z$ in $4_z/m_z m_x m_{xy}$, *i.e.* to the index of $m_x m_y m_z$ in $4_z/m_z m_x m_{xy}$, $n_a = [4_z/m_z m_x m_{xy} : m_x m_y m_z] = |4_z/m_z m_x m_{xy}| : |m_x m_y m_z| = 16 : 8 = 2$, and the number d_a of principal domain states in one ferroelastic domain state is equal to the index of $2_x m_y m_z$ in $m_x m_y m_z$, *i.e.* $d_a = [m_x m_y m_z : 2_x m_y m_z] = |m_x m_y m_z| : |2_x m_y m_z| = 8 : 4 = 2$.

A generalization of these considerations, performed in Section 3.2.3.3.5 (see especially Proposition 3.2.3.30 and Examples 3.2.3.10 and 3.2.3.33), yields the following main results. Assume that $\lambda^{(1)}$ is a secondary order parameter of a transition with symmetry descent $G \supset F_1$. Then the stabilizer L_1 of this parameter $I_G(\lambda^{(1)}) \equiv L_1$ is an intermediate group,

$$F_1 \subseteq I_G(\lambda^{(1)}) \equiv L_1 \subseteq G. \quad (3.4.2.16)$$

Lattices of subgroups in Figs. 3.1.3.1 and 3.1.3.2 are helpful in checking this condition.

The set of n principal domain states (the orbit $G\mathbf{S}_1$) splits into n_λ subsets

$$n_\lambda = [G : L_1] = |G| : |L_1|. \quad (3.4.2.17)$$

Each of these subsets consists of d_λ principal domain states,

$$d_\lambda = [L_1 : F_1] = |L_1| : |F_1|. \quad (3.4.2.18)$$

The number d_λ is called a *degeneracy of secondary domain states*.

The product of numbers n_λ and d_λ is equal to the number n of principal domain states [see equation (3.2.3.26)]:

$$n_\lambda d_\lambda = n. \quad (3.4.2.19)$$

Principal domain states from each subset have the same value of the secondary order parameter $\lambda^{(j)}, j = 1, 2, \ldots, n_\lambda$ and any two principal domain states from different subsets have different values of $\lambda^{(j)}$. A state of the crystal with a given value of the secondary order parameter $\lambda^{(j)}$ will be called a *secondary domain state* $\mathbf{R}_j, j = 1, 2, \ldots, n_\lambda$. Equivalent terms are *degenerate* or *compound domain state*.

In a limiting case $L_1 = F_1$, the parameter $\lambda^{(1)}$ is identical with the principal tensor parameter and there is no degeneracy, $d_\lambda = 1$.

Secondary domain states $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_j, \ldots, \mathbf{R}_{n_\lambda}$ are in a one-to-one correspondence with left cosets of L_1 in the decomposition

$$G = h_1 L_1 \cup h_2 L_1 \cup \ldots \cup h_j L_1 \cup \ldots \cup h_{n_\lambda} L_1, \quad (3.4.2.20)$$

therefore

$$\mathbf{R}_j = h_j \mathbf{R}_1, \quad j = 1, 2, \ldots, n_\lambda. \quad (3.4.2.21)$$

Principal domain states of the first secondary domain state $\mathbf{R}_1$ can be determined from the first principal domain state $\mathbf{S}_1$:

$$\mathbf{S}_k = p_k \mathbf{S}_1, \quad k = 1, 2, \ldots, d_\lambda, \quad (3.4.2.22)$$

where p_k is the representative of the kth left coset of F_1 of the decomposition

$$L_1 = p_1 F_1 \cup p_2 F_1 \cup \ldots \cup p_k F_1 \cup \ldots \cup p_{d_\lambda} F_1. \quad (3.4.2.23)$$

The partition of principal domain states according to a secondary order parameter offers a convenient labelling of principal domain states by two indices j, k, where the first index j denotes the sequential number of the secondary domain state and the second index k gives the sequential number of the principal domain state within the jth secondary domain state [see equation (3.2.3.79)]:

$$\mathbf{S}_{jk} = h_j p_k \mathbf{S}_{11}, \quad \mathbf{S}_{11} = \mathbf{S}_1, \quad j = 1, 2, \ldots, n_\lambda, \quad k = 1, 2, \ldots, d_\lambda, \quad (3.4.2.24)$$

where h_j and p_k are representatives of the decompositions (3.4.2.20) and (3.4.2.23), respectively.

The secondary order parameter λ can be identified with a principal order parameter of a phase transition with symmetry descent $G \subset L_1$ (see Section 3.4.2.3). The concept of secondary domain states enables one to define domain states that are characterized by a certain spontaneous property. We present the three most significant cases of such ferroic domain states.

3.4.2.2.1. *Ferroelastic domain state*

The distinction ferroelastic–non-ferroelastic is a basic division in domain structures. *Ferroelastic transitions* are ferroic transi-