

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

sion for the disorientation angle (obliquity) and other data. Table 3.4.3.7 lists representatives of all classes of ferroelastic domain pairs for which *no compatible domain walls* exist. Since Table 3.4.2.7 contains for each symmetry descent $G \supset F$ all twinning groups that specify different G -orbits of domain pairs which can appear in the ferroic phase, one can get from this table and from Tables 3.4.3.4, 3.4.3.6 and 3.4.3.7 the significant features of the domain structure of any ferroic phase.

3.4.3.1. Domain pairs and their symmetry, twin law

A pair of two domain states, in short a *domain pair*, consists of two domain states, say \mathbf{S}_i and \mathbf{S}_k , that are considered irrespective of their possible coexistence (Janovec, 1972). Geometrically, domain pairs can be visualized as two interpenetrating structures of \mathbf{S}_i and \mathbf{S}_k . Algebraically, two domain states \mathbf{S}_i and \mathbf{S}_k can be treated in two ways: as an ordered or an unordered pair (see Section 3.2.3.1.2).

An *ordered domain pair*, denoted $(\mathbf{S}_i, \mathbf{S}_k)$, consists of the first domain state \mathbf{S}_i and the second domain state. Occasionally, it is convenient to consider a *trivial ordered domain pair* $(\mathbf{S}_i, \mathbf{S}_i)$ composed of two identical domain states \mathbf{S}_i .

An ordered domain pair is a construct that in bicrystallography is called a *dichromatic complex* (see Section 3.3.3; Pond & Vlachavas, 1983; Sutton & Balluffi, 1995; Wadhawan, 2000).

An ordered domain pair $(\mathbf{S}_i, \mathbf{S}_k)$ is defined by specifying \mathbf{S}_i and \mathbf{S}_k or by giving \mathbf{S}_i and a *switching operation* g_{ik} that transforms \mathbf{S}_i into \mathbf{S}_k ,

$$\mathbf{S}_k = g_{ik}\mathbf{S}_i, \quad \mathbf{S}_i, \mathbf{S}_k \in GS_1, \quad g_{ik} \in G. \quad (3.4.3.1)$$

For a given \mathbf{S}_i and \mathbf{S}_k , the switching operation g_{ik} is not uniquely defined since each operation from the left coset $g_{ik}F_i$ [where F_i is the stabilizer (symmetry group) of \mathbf{S}_i] transforms \mathbf{S}_i into \mathbf{S}_k , $g_{ik}\mathbf{S}_i = (g_{ik}F_i)\mathbf{S}_i = \mathbf{S}_k$.

An ordered domain pair $(\mathbf{S}_k, \mathbf{S}_i)$ with a reversed order of domain states is called a *transposed domain pair* and is denoted $(\mathbf{S}_i, \mathbf{S}_k)^t \equiv (\mathbf{S}_k, \mathbf{S}_i)$. A non-trivial ordered domain pair $(\mathbf{S}_i, \mathbf{S}_k)$ is different from the transposed ordered domain pair,

$$(\mathbf{S}_k, \mathbf{S}_i) \neq (\mathbf{S}_i, \mathbf{S}_k) \text{ for } i \neq k. \quad (3.4.3.2)$$

If g_{ik} is a switching operation of an ordered domain pair $(\mathbf{S}_i, \mathbf{S}_k)$, then the inverse operation g_{ik}^{-1} of g_{ik} is a switching operation of the transposed domain pair $(\mathbf{S}_k, \mathbf{S}_i)$:

$$\text{if } (\mathbf{S}_i, \mathbf{S}_k) = (\mathbf{S}_i, g_{ik}\mathbf{S}_i) \text{ and } (\mathbf{S}_k, \mathbf{S}_i) = (\mathbf{S}_k, g_{ki}\mathbf{S}_k), \text{ then } g_{ki} = g_{ik}^{-1}. \quad (3.4.3.3)$$

An *unordered domain pair*, denoted by $\{\mathbf{S}_i, \mathbf{S}_k\}$, is defined as an *unordered* set consisting of two domain states \mathbf{S}_i and \mathbf{S}_k . In this case, the sequence of domains states in a domain pair is irrelevant, therefore

$$\{\mathbf{S}_i, \mathbf{S}_k\} = \{\mathbf{S}_k, \mathbf{S}_i\}. \quad (3.4.3.4)$$

In what follows, we shall omit the specification ‘ordered’ or ‘unordered’ if it is evident from the context, or if it is not significant.

A domain pair $(\mathbf{S}_i, \mathbf{S}_k)$ can be transformed by an operation $g \in G$ into another domain pair,

$$g(\mathbf{S}_i, \mathbf{S}_k) \equiv (g\mathbf{S}_i, g\mathbf{S}_k) = (\mathbf{S}_l, \mathbf{S}_m), \quad \mathbf{S}_i, \mathbf{S}_k, \mathbf{S}_l, \mathbf{S}_m \in GS_1, \quad g \in G. \quad (3.4.3.5)$$

These two domain pairs will be called *crystallographically equivalent (in G) domain pairs* and will be denoted $(\mathbf{S}_i, \mathbf{S}_k) \stackrel{G}{\sim} (\mathbf{S}_l, \mathbf{S}_m)$.

If the transformed domain pair is a transposed domain pair $(\mathbf{S}_k, \mathbf{S}_i)$, then the operation g will be called a *transposing operation*,

$$g^*(\mathbf{S}_i, \mathbf{S}_k) = (g^*\mathbf{S}_i, g^*\mathbf{S}_k) = (\mathbf{S}_k, \mathbf{S}_i), \quad \mathbf{S}_i, \mathbf{S}_k \in GS_1, \quad g^* \in G. \quad (3.4.3.6)$$

We see that a transposing operation $g^* \in G$ exchanges domain states \mathbf{S}_i and \mathbf{S}_k :

$$g^*\mathbf{S}_i = \mathbf{S}_k, \quad g^*\mathbf{S}_k = \mathbf{S}_i, \quad \mathbf{S}_i, \mathbf{S}_k \in GS_1, \quad g^* \in G. \quad (3.4.3.7)$$

Thus, comparing equations (3.4.3.1) and (3.4.3.7), we see that a transposing operation g^* is a switching operation that transforms \mathbf{S}_i into \mathbf{S}_k , and, in addition, switches \mathbf{S}_k into \mathbf{S}_i . Then a product of two transposing operations is an operation that changes neither \mathbf{S}_i nor \mathbf{S}_k .

What we call in this chapter a *transposing operation* is usually denoted as a *twin operation* (see Section 3.3.5 and *e.g.* Holser, 1958a; Curien & Donnay, 1959; Koch, 2004). We are reserving the term ‘twin operation’ for operations that exchange domain states of a simple domain twin in which two ferroelastic domain states *coexist* along a domain wall. Then, as we shall see, the transposing operations are identical with the twin operations in non-ferroelastic domains (see Section 3.4.3.5) but may differ in ferroelastic domain twins, where only some transposing operations of a single-domain pair survive as twin operations of the corresponding ferroelastic twin with a nonzero disorientation angle (see Section 3.4.3.6.3).

Transposing operations are marked in this chapter by a star, * (with five points), which should be distinguished from an asterisk, * (with six points), used to denote operations or symmetry elements in reciprocal space. The same designation is used in the software *GI★KoBo-1* and in the tables in Kopský (2001). A prime, ′, is often used to designate transposing (twin) operations (see Section 3.3.5; Curien & Le Corre, 1958; Curien & Donnay, 1959). We have reserved the prime for operations involving time inversion, as is customary in magnetism (see Chapter 1.5). This choice allows one to analyse domain structures in magnetic and magnetoelectric materials (see *e.g.* Přívratská & Janovec, 1997).

In connection with this, we invoke the notion of a *twin law*. Since this term is not yet common in the context of domain structures, we briefly explain its meaning.

In crystallography, a twin is characterized by a twin law defined in the following way (see Section 3.3.2; Koch, 2004; Cahn, 1954):

(i) A *twin law* describes the geometrical relation between twin components of a twin. This relation is expressed by a *twin operation* that brings one of the twin components into parallel orientation with the other, and *vice versa*. A symmetry element corresponding to the twin operation is called the *twin element*. (Requirement ‘and *vice versa*’ is included in the definition of Cahn but not in that of Koch; for the most common twin operations of the second order the ‘*vice versa*’ condition is fulfilled automatically.)

(ii) The relation between twin components deserves the name ‘twin law’ only if it occurs frequently, is reproducible and represents an inherent feature of the crystal.

An analogous definition of a *domain twin law* can be formulated for domain twins by replacing the term ‘twin components’ by ‘domains’, say $\mathbf{D}_i(\mathbf{S}_j, Q_k)$ and $\mathbf{D}_m(\mathbf{S}_n, Q_p)$, where \mathbf{S}_j, Q_k and \mathbf{S}_n, Q_p are, respectively, the domain state and the domain region of the domains $\mathbf{D}_i(\mathbf{S}_j, Q_k)$ and $\mathbf{D}_m(\mathbf{S}_n, Q_p)$, respectively (see Section 3.4.2.1). The term ‘transposing operation’ corresponds to transposing operation g_{12}^* of domain pair $(\mathbf{S}_1, \mathbf{S}_2) = (\mathbf{S}_j, g_{jn}^*\mathbf{S}_n)$ as we have defined it above if two domains with domain states \mathbf{S}_1 and \mathbf{S}_2 *coexist* along a domain wall of the domain twin.

Domain twin laws can be conveniently expressed by crystallographic groups. This specification is simpler for non-ferroelastic twins, where a twin law can be expressed by a dichromatic space group (see Section 3.4.3.5), whereas for ferroelastic twins with a compatible domain wall dichromatic layer groups are adequate (see Section 3.4.3.6.3).

3.4. DOMAIN STRUCTURES

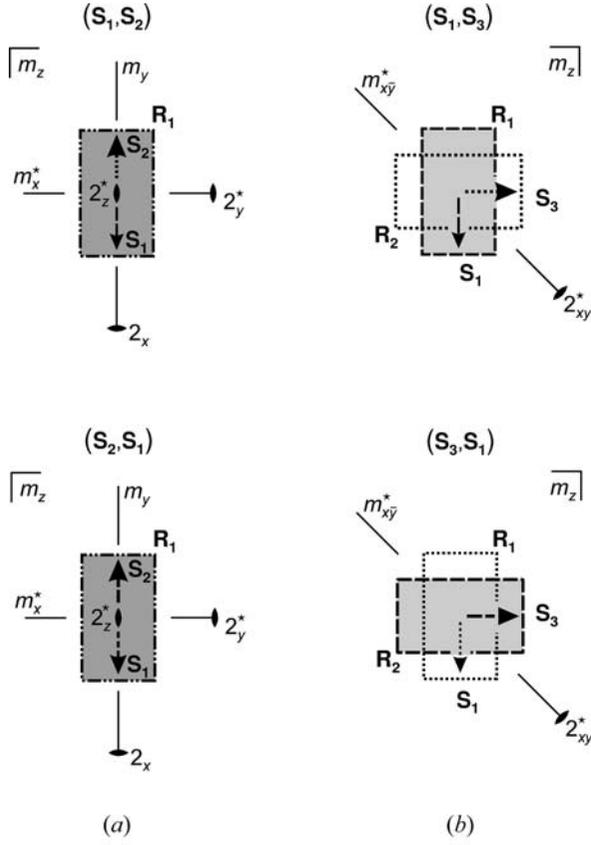


Fig. 3.4.3.1. Transposable domain pairs. Single-domain states are those from Fig. 3.4.2.2. (a) Completely transposable non-ferroelastic domain pair. (b) Partially transposable ferroelastic domain pair.

Restriction (ii), formulated by Georges Friedel (1926) and explained in detail by Cahn (1954), expresses a necessity to exclude from considerations crystal aggregates (intergrowths) with approximate or accidental ‘nearly exact’ crystal components resembling twins (Friedel’s *macles d’imagination*) and thus to restrict the definition to ‘true twins’ that fulfil condition (i) exactly and are characteristic for a given material. If we confine our considerations to domain structures that are formed from a *homogeneous* parent phase, this requirement is fulfilled for *all* aggregates consisting of two or more domains. Then the definition of a ‘domain twin law’ is expressed only by condition (i). Condition (ii) is important for growth twins.

We should note that the definition of a twin law given above involves only domain states and does not explicitly contain specification of the contact region between twin components or neighbouring domains. The concept of domain state is, therefore, relevant for discussing the twin laws. Moreover, there is no requirement on the coexistence of interpenetrating structures in a domain pair. One can even, therefore, consider cases where no real coexistence of both structures is possible. Nevertheless, we note that the characterization of twin laws used in mineralogy often includes specification of the contact region (*e.g.* twin plane or diffuse region in penetrating twins).

Ordered domain pairs (S_1, S_2) and (S_1, S_3) , formed from domain states of our illustrative example (see Fig. 3.4.2.2), are displayed in Fig. 3.4.3.1(a) and (b), respectively, as two superposed rectangles with arrows representing spontaneous polarization. In ordered domain pairs, the first and the second domain state are distinguished by shading [the first domain state is grey (‘black’) and the second clear (‘white’)] and/or by using dashed and dotted lines for the first and second domain state, respectively.

In Fig. 3.4.3.2, the ordered domain pair (S_1, S_2) and the transposed domain pair (S_2, S_1) are depicted in a similar way for

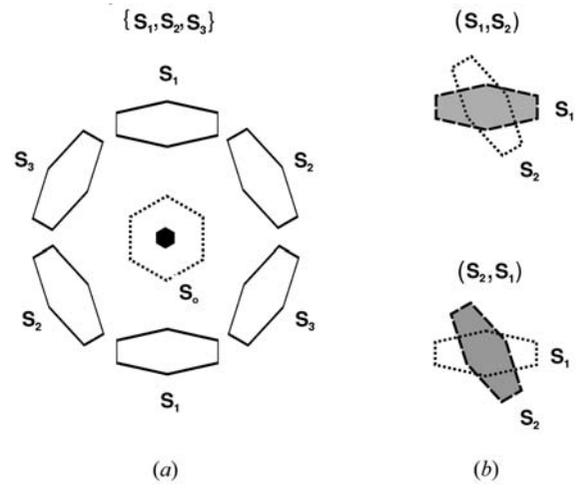


Fig. 3.4.3.2. Non-transposable domain pairs. (a) The parent phase with symmetry $G = 6_z/m_z$ is represented by a dotted hexagon and the three ferroelastic single-domain states with symmetry $F_1 = F_2 = F_3 = 2_z/m_z$ are depicted as drastically squeezed hexagons. (b) Domain pair (S_1, S_2) and transposed domain pair (S_2, S_1) . There exists no operation from the group $6_z/m_z$ that would exchange domain states S_1 and S_2 , *i.e.* that would transform one domain pair into a transposed domain pair.

another example with symmetry descent $G = 6_z/m_z \supset 2_z/m_z = F_1$.

Let us now examine the *symmetry of domain pairs*. The *symmetry group* F_{ik} of an ordered domain pair $(S_i, S_k) = (S_i, g_{ik}S_i)$ consists of all operations that leave invariant both S_i and S_k , *i.e.* F_{ik} comprises all operations that are common to stabilizers (symmetry groups) F_i and F_k of domain states S_i and S_k , respectively,

$$F_{ik} \equiv F_i \cap F_k = F_i \cap g_{ik}F_i g_{ik}^{-1}, \quad (3.4.3.8)$$

where the symbol \cap denotes the intersection of groups F_i and F_k . The group F_{ik} is in Section 3.3.4 denoted by \mathcal{H}^* and is called an intersection group.

From equation (3.4.3.8), it immediately follows that the symmetry F_{ki} of the transposed domain pair (S_k, S_i) is the same as the symmetry F_{ik} of the initial domain pair (S_i, S_k) :

$$F_{ki} = F_k \cap F_i = F_i \cap F_k = F_{ik}. \quad (3.4.3.9)$$

Symmetry operations of an unordered domain pair $\{S_i, S_k\}$ include, besides operations of F_{ik} that do not change either S_i or S_k , all transposing operations, since for an unordered domain pair a transposed domain pair is identical with the initial domain pair [see equation (3.4.3.4)]. If g_{ik}^* is a transposing operation of (S_i, S_k) , then all operations from the left coset $g_{ik}^*F_{ik}$ are transposing operations of that domain pair as well. Thus the *symmetry group* J_{ik} of an unordered domain pair $\{S_i, S_k\}$ can be, in a general case, expressed in the following way:

$$J_{ik} = F_{ik} \cup g_{ik}^*F_{ik}, \quad g_{ik}^* \in G. \quad (3.4.3.10)$$

Since, for an unordered domain, the order of domain states in a domain pair is not significant, the transposition of indices i, k in J_{ik} does not change this group,

$$J_{ik} = F_{ik} \cup g_{ik}^*F_{ik} = F_{ki} \cup g_{ki}^*F_{ki} = J_{ki}, \quad (3.4.3.11)$$

which also follows from equations (3.4.3.3) and (3.4.3.9).

A *basic classification of domain pairs* follows from their symmetry. Domain pairs for which at least one transposing operation exists are called *transposable* (or *ambivalent*) *domain pairs*. The symmetry group of a transposable unordered domain pair (S_i, S_k) is given by equation (3.4.3.10).

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

The star in the symbol J_{ik}^* indicates that this group contains transposing operations, *i.e.* that the corresponding domain pair $(\mathbf{S}_i, \mathbf{S}_k)$ is a transposable domain pair.

A transposable domain pair $(\mathbf{S}_i, \mathbf{S}_k)$ and transposed domain pair $(\mathbf{S}_k, \mathbf{S}_i)$ belong to the same G -orbit:

$$G(\mathbf{S}_i, \mathbf{S}_k) = G(\mathbf{S}_k, \mathbf{S}_i). \quad (3.4.3.12)$$

If $\{\mathbf{S}_i, \mathbf{S}_k\}$ is a transposable pair and, moreover, $F_i = F_k = F_{ik}$, then *all* operations of the left coset $g_{ik}^* F_i$ simultaneously switch \mathbf{S}_i into \mathbf{S}_k and \mathbf{S}_k into \mathbf{S}_i . We call such a pair a *completely transposable domain pair*. The symmetry group J_{ik} of a completely transposable pair $\{\mathbf{S}_i, \mathbf{S}_k\}$ is

$$J_{ik}^* = F_i \cup g_{ik}^* F_i, \quad g_{ik}^* \in G, \quad F_i = F_k. \quad (3.4.3.13)$$

We shall use for symmetry groups of completely transposable domain pairs the symbol J_{ik}^* .

If $F_i \neq F_k$, then $F_{ik} \subset F_i$ and the number of transposing operations is smaller than the number of operations switching \mathbf{S}_i into \mathbf{S}_k . We therefore call such pairs *partially transposable domain pairs*. The symmetry group J_{ik} of a partially transposable domain pair $\{\mathbf{S}_i, \mathbf{S}_k\}$ is given by equation (3.4.3.10).

The symmetry groups J_{ik} and J_{ik}^* , expressed by (3.4.3.10) or by (3.4.3.13), respectively, consists of two left cosets only. The first is equal to F_{ik} and the second one $g_{ik}^* F_{ik}$ comprises all the transposing operations marked by a star. An explicit symbol $J_{ik}(F_{ik})$ of these groups contains both the group J_{ik} and F_{ik} , which is a subgroup of J_{ik} of index 2.

If one 'colours' one domain state, *e.g.* \mathbf{S}_i , 'black' and the other, *e.g.* \mathbf{S}_k , 'white', then the operations without a star can be interpreted as 'colour-preserving' operations and operations with a star as 'colour-exchanging' operations. Then the group $J_{ik}(F_{ik})$ can be treated as a 'black-and-white' or dichromatic group (see Section 3.2.3.2.7). These groups are also called Shubnikov groups (Bradley & Cracknell, 1972), two-colour or Heesch-Shubnikov groups (Opechowski, 1986), or antisymmetry groups (Vainshtein, 1994).

The advantage of this notation is that instead of an explicit symbol $J_{ik}(F_{ik})$, the symbol of a dichromatic group specifies both the group J_{ik} and the subgroup F_{ij} or F_1 , and thus also the transposing operations that define, according to equation (3.4.3.7), the second domain state \mathbf{S}_j of the pair.

We have agreed to use a special symbol J_{ik}^* only for completely transposable domain pairs. Then the star in this case indicates that the subgroup F_{ik} is equal to the symmetry group of the first domain state \mathbf{S}_i in the pair, $F_{ik} = F_i$. Since the group F_i is usually well known from the context (in our main tables it is given in the first column), we no longer need to add it to the symbol of J_{ik} .

Domain pairs for which an exchanging operation g_{ik}^* cannot be found are called *non-transposable* (or *polar*) *domain pairs*. The symmetry J_{ij} of a non-transposable domain pair is reduced to the usual 'monochromatic' symmetry group F_{ik} of the corresponding ordered domain pair $(\mathbf{S}_i, \mathbf{S}_k)$. The G -orbits of mutually transposed polar domain pairs are disjoint (Janovec, 1972):

$$G(\mathbf{S}_i, \mathbf{S}_k) \cap G(\mathbf{S}_k, \mathbf{S}_i) = \emptyset. \quad (3.4.3.14)$$

Transposed polar domain pairs, which are always non-equivalent, are called *complementary domain pairs*.

If, in particular, $F_{ik} = F_i = F_k$, then the symmetry group of the unordered domain pair is

$$J_{ik} = F_i = F_k. \quad (3.4.3.15)$$

In this case, the unordered domain pair $\{\mathbf{S}_i, \mathbf{S}_k\}$ is called a *non-transposable simple domain pair*.

If $F_i \neq F_k$, then the number of operations of F_{ik} is smaller than that of F_i and the symmetry group J_{ik} is equal to the symmetry group F_{ik} of the ordered domain pair $(\mathbf{S}_i, \mathbf{S}_k)$,

$$J_{ik} = F_{ik}, \quad F_{ik} \subset F_i. \quad (3.4.3.16)$$

Such an unordered domain pair $\{\mathbf{S}_i, \mathbf{S}_k\}$ is called a *non-transposable multiple domain pair*. The reason for this designation will be given later in this section.

We stress that domain states forming a domain pair are not restricted to single-domain states. Any two domain states with a defined orientation in the coordinate system of the parent phase can form a domain pair for which all definitions given above are applicable.

Example 3.4.3.1. Now we examine domain pairs in our illustrative example of a phase transition with symmetry descent $G = 4_z/m_z m_x m_{xy} \supset 2_x m_y m_z = F_1$ and with four single-domain states $\mathbf{S}_1, \mathbf{S}_2, \mathbf{S}_3$ and \mathbf{S}_4 , which are displayed in Fig. 3.4.2.2. The domain pair $\{\mathbf{S}_1, \mathbf{S}_2\}$ depicted in Fig. 3.4.3.1(a) is a completely transposable domain pair since transposing operations exist, *e.g.* $g_{12}^* = m_x^*$, and the symmetry group F_{12} of the ordered domain pair $(\mathbf{S}_1, \mathbf{S}_2)$ is

$$F_{12} = F_1 \cap F_2 = F_1 = F_2 = 2_x m_y m_z. \quad (3.4.3.17)$$

The symmetry group J_{12} of the unordered pair $\{\mathbf{S}_1, \mathbf{S}_2\}$ is a dichromatic group,

$$J_{12}^* = 2_x m_y m_z \cup m_x^* \{2_x m_y m_z\} = m_x^* m_y m_z. \quad (3.4.3.18)$$

The domain pair $\{\mathbf{S}_1, \mathbf{S}_3\}$ in Fig. 3.4.3.1(b) is a partially transposable domain pair, since there are operations exchanging domain states \mathbf{S}_1 and \mathbf{S}_3 , *e.g.* $g_{13}^* = m_{xy}^*$, but the symmetry group F_{13} of the ordered domain pair $(\mathbf{S}_1, \mathbf{S}_3)$ is smaller than F_1 :

$$F_{13} = F_1 \cap F_3 = 2_x m_y m_z \cap m_x 2_y m_z = \{1, m_z\} \equiv \{m_z\}, \quad (3.4.3.19)$$

where 1 is an identity operation and $\{1, m_z\}$ denotes the group m_z . The symmetry group of the unordered domain pair $\{\mathbf{S}_1, \mathbf{S}_3\}$ is equal to a dichromatic group,

$$J_{13} = \{m_z\} \cup 2_{xy}^* \{m_z\} = 2_{xy}^* m_{xy}^* m_z. \quad (3.4.3.20)$$

The domain pair $(\mathbf{S}_1, \mathbf{S}_2)$ in Fig. 3.4.3.2(b) is a non-transposable simple domain pair, since there is no transposing operation of $G = 6_z/m_z$ that would exchange domain states \mathbf{S}_1 and \mathbf{S}_2 , and $F_1 = F_2 = 2_z/m_z$. The symmetry group J_{12} of the unordered domain pair $\{\mathbf{S}_1, \mathbf{S}_2\}$ is a 'monochromatic' group,

$$J_{12} = F_{12} = F_1 = F_2 = 2_z/m_z. \quad (3.4.3.21)$$

The G -orbit $6_z/m_z(\mathbf{S}_1, \mathbf{S}_2)$ of the pair $(\mathbf{S}_1, \mathbf{S}_2)$ has no common domain pair with the G -orbit $6_z/m_z(\mathbf{S}_2, \mathbf{S}_1)$ of the transposed domain pair $(\mathbf{S}_2, \mathbf{S}_1)$. These two 'complementary' orbits contain mutually transposed domain pairs.

Symmetry groups of domain pairs provide a basic classification of domain pairs into the four types introduced above. This classification applies to microscopic domain pairs as well.

3.4.3.2. Twinning group, distinction of two domain states

We have seen that for transposable domain pairs the symmetry group J_{ij} of a domain pair $(\mathbf{S}_i, \mathbf{S}_j)$ specifies transposing operations $g_{ij}^* F_i$ that transform \mathbf{S}_i into \mathbf{S}_j . This does not apply to non-transposable domain pairs, where the symmetry group $J_{ij} = F_{ij}$ does not contain any switching operation. Another group exists, called the *twinning group*, which is associated with a domain pair and which does not have this drawback. The twinning group determines the distinction of two domain states, specifies the external fields needed to switch one domain state into another one and enables one to treat domain pairs independently of the transition $G \supset F_1$. This facilitates the tabulation of the properties of non-equivalent domain pairs that appear in all possible ferroic phases.