International Tables for Crystallography (2013). Vol. D, Section 3.4.3.3, pp. 510–511.

principal tensors are: $\kappa_2^{(1)} = (g_4, 0)$, $\kappa_3^{(1)} = (d_{11}, 0)$, $\kappa_4^{(1)} = (d_{12}, 0)$, $\kappa_5^{(1)} = (d_{13}, 0)$, $\kappa_6^{(1)} = (d_{26}, 0)$, $\kappa_7^{(1)} = (d_{35}, 0)$ (the physical meaning of the components is explained in Table 3.4.3.5). In the domain state $\mathbf{S}_3$ they keep their absolute value but appear as the second nonzero components, as with spontaneous polarization.

There is an intermediate group $L_{13} = m_x m_y m_z$ between $F_1 = 2_x m_y m_z$ and $K_{13} = 4_z/m_z m_x m_{xy}$, since $L_{13} = m_x m_y m_z$ does not contain $g_{13} = 2_{xy}$. The one-dimensional secondary tensor parameters for the symmetry descent $K_{13} = 4_z/m_z m_x m_{xy} \supset L_{13} = m_x m_y m_z$ was also found in Example 3.4.2.4: $\lambda_1^{(1)} = u_1 - u_2$; $\lambda_2^{(1)} = A_{14} + A_{25}, A_{36}$; $\lambda_3^{(1)} = s_{11} - s_{22}, s_{13} - s_{23}, s_{44} - s_{55}$; $\lambda_4^{(1)} = Q_{11} - Q_{22}, Q_{12} - Q_{21}, Q_{13} - Q_{23}, Q_{31} - Q_{32}, Q_{44} - Q_{55}$. All these parameters have the opposite sign in $\mathbf{S}_3$.

The tensor distinction of two domain states $\mathbf{S}_1$ and $\mathbf{S}_j$ in a domain pair $(\mathbf{S}_1, \mathbf{S}_j)$ provides a useful *classification of domain pairs* given in the second and the third columns of Table 3.4.3.1. This classification can be extended to ferroic phases which are named according to domain pairs that exist in this phase. Thus, for example, if a ferroic phase contains ferroelectric (ferroelastic) domain pair(s), then this phase is a ferroelectric (ferroelastic) phase. Finer division into full and partial ferroelectric (ferroelastic) phases specifies whether all or only some of the possible domain pairs in this phase are ferroelectric (ferroelastic) ones. Another approach to this classification uses the notions of principal and secondary tensor parameters, and was explained in Section 3.4.2.2.

A discussion of and many examples of secondary ferroic phases are available in papers by Newnham & Cross (1974*a*,*b*) and Newnham & Skinner (1976), and tertiary ferroic phases are discussed by Amin & Newnham (1980).

We shall now show that the tensor distinction of domain states is closely related to the switching of domain states by external fields.

3.4.3.3. *Switching of ferroic domain states*

We saw in Section 3.4.2.1 that all domain states of the orbit $G\mathbf{S}_1$ have the same chance of appearing. This implies that they have the same free energy, *i.e.* they are degenerate. The same conclusion follows from thermodynamic theory, where domain states appear as equivalent solutions of equilibrium values of the order parameter, *i.e.* all domain states exhibit the same free energy Ψ (see Section 3.1.2). These statements hold under a tacit assumption of absent external electric and mechanical fields. If these fields are nonzero, the degeneracy of domain states can be partially or completely lifted.

The free energy $\Psi^{(k)}$ per unit volume of a ferroic domain state $\mathbf{S}_k$, $k = 1, 2, \ldots, n$, with spontaneous polarization $\mathbf{P}_0^{(k)}$ with components $P_{0i}^{(k)}$, $i = 1, 2, 3$, and with spontaneous strain components $u_{0\mu}^{(k)}$, $\mu = 1, 2, \ldots, 6$, is (Aizu, 1972)

$$\Psi^{(k)} = \Psi_0 - P_{0i}^{(k)} E_i - u_{0\mu}^{(k)} \sigma_\mu - d_{i\mu}^{(k)} E_i \sigma_\mu - \tfrac{1}{2} \varepsilon_0 \kappa_{ik}^{(k)} E_i E_k - \tfrac{1}{2} s_{\mu\nu}^{(k)} \sigma_\mu \sigma_\nu - \tfrac{1}{2} Q_{ik\mu} E_i E_k \sigma_\mu - \ldots, \quad (3.4.3.32)$$

where the Einstein summation convention (summation with respect to suffixes that occur twice in the same term) is used with $i, j = 1, 2, 3$ and $\mu, \nu = 1, 2, \ldots, 6$. The symbols in equation (3.4.3.32) have the following meaning: E_i and u_μ are components of the external electric field and of the mechanical stress, respectively, $d_{i\mu}^{(k)}$ are components of the piezoelectric tensor, $\varepsilon_0 \kappa_{ij}^{(k)}$ are components of the electric susceptibility, $s_{\mu\nu}^{(k)}$ are compliance components, and $Q_{ij\mu}^{(k)}$ are components of electrostriction (components with Greek indices are expressed in matrix notation) [see Section 3.4.5 (Glossary), Chapter 1.1 or Nye (1985); Sirotin & Shaskolskaya (1982)].

We shall examine two domain states $\mathbf{S}_1$ and $\mathbf{S}_j$, *i.e.* a domain pair $(\mathbf{S}_1, \mathbf{S}_j)$, in electric and mechanical fields. The difference of their free energies is given by

$$\begin{aligned}\Psi^{(j)} - \Psi^{(1)} = {} & -(P_{0i}^{(j)} - P_{0i}^{(1)}) E_i - (u_{0\mu}^{(j)} - u_{0\mu}^{(1)}) \sigma_\mu - (d_{i\mu}^{(j)} - d_{i\mu}^{(1)}) E_i \sigma_\mu \\ & - \tfrac{1}{2} \varepsilon_0 (\kappa_{ik}^{(j)} - \kappa_{ik}^{(1)}) E_i E_k - \tfrac{1}{2} (s_{\mu\nu}^{(j)} - s_{\mu\nu}^{(1)}) \sigma_\mu \sigma_\nu \\ & - \tfrac{1}{2} (Q_{ik\mu}^{(j)} - Q_{ik\mu}^{(1)}) E_i E_k \sigma_\mu - \ldots . \end{aligned} \quad (3.4.3.33)$$

For a domain pair $(\mathbf{S}_1, \mathbf{S}_j)$ and given external fields, there are three possibilities:

(1) $\Psi^{(j)} = \Psi^{(1)}$. Domain states $\mathbf{S}_1$ and $\mathbf{S}_j$ can coexist in equilibrium in given external fields.

(2) $\Psi^{(j)} < \Psi^{(1)}$. In given external fields, domain state $\mathbf{S}_j$ is more stable than $\mathbf{S}_1$; for large enough fields (higher than the coercive ones), the state $\mathbf{S}_1$ switches into the state $\mathbf{S}_j$.

(3) $\Psi^{(j)} > \Psi^{(1)}$. In given external fields, domain state $\mathbf{S}_j$ is less stable than $\mathbf{S}_1$; for large enough fields (higher than the coercive ones), the state $\mathbf{S}_j$ switches into the state $\mathbf{S}_1$.

A typical dependence of applied stress and corresponding strain in ferroelastic materials has a form of a elastic hysteresis loop (see Fig. 3.4.1.3). Similar dielectric hysteresis loops are observed in ferroelectric materials; examples can be found in books on ferroelectric crystals (*e.g.* Jona & Shirane, 1962).

A classification of switching (state shifts in Aizu's terminology) based on equation (3.4.3.33) was put forward by Aizu (1972, 1973) and is summarized in the second and fourth columns of Table 3.4.3.1. The order of the state shifts specifies the switching fields that are necessary for switching one domain state of a domain pair into the second state of the pair.

Another distinction related to switching distinguishes between *actual* and *potential* ferroelectric (ferroelastic) phases, depending on whether or not it is possible to switch the spontaneous polarization (spontaneous strain) by applying an electric field (mechanical stress) lower than the electrical (mechanical) breakdown limit under reasonable experimental conditions

Table 3.4.3.1. *Classification of domain pairs, ferroic phases and of switching (state shifts)*

$P_{0i}^{(k)}$ and $u_{0\mu}^{(k)}$ are components of the spontaneous polarization and spontaneous strain in the domain state $\mathbf{S}_k$, where $k = 1$ or $k = j$; similarly, $d_{i\mu}^{(k)}$ are components of the piezoelectric tensor, $\varepsilon_0 \kappa_{ij}^{(k)}$ are components of electric susceptibility, $s_{\mu\nu}^{(k)}$ are compliance components and $Q_{ij\mu}^{(k)}$ are components of electrostriction (components with Greek indices are expressed in matrix notation) [see Chapter 1.1 or *e.g.* Nye (1985) and Sirotin & Shaskolskaya (1982)]. Text in italics concerns the classification of ferroic phases. $\mathbf{E}$ is the electric field and σ is the mechanical stress.

Ferroic class	Domain pair – *at least in one pair*	Domain pair – *phase*	Switching (state shift)	Switching field
Primary	At least one $P_{0i}^{(j)} - P_{0i}^{(1)} \neq 0$	Ferroelectric	Electrically first order	$\mathbf{E}$
	At least one $u_{0\mu}^{(j)} - u_{0\mu}^{(1)} \neq 0$	Ferroelastic	Mechanically first order	σ
Secondary	At least one $P_{0i}^{(j)} - P_{0i}^{(1)} \neq 0$ and at least one $u_{0\mu}^{(j)} - u_{0\mu}^{(1)} \neq 0$	Ferroelastoelectric	Electromechanically first order	$\mathbf{E}\sigma$
	All $P_{0i}^{(j)} - P_{0i}^{(1)} = 0$ and at least one $\varepsilon_0(\kappa_{ik}^{(j)} - \kappa_{ik}^{(1)}) \neq 0$	Ferrobielectric	Electrically second order	$\mathbf{EE}$
	All $u_{0\mu}^{(j)} - u_{0\mu}^{(1)} = 0$ and at least one $s_{\mu\nu}^{(j)} - s_{\mu\nu}^{(1)} \neq 0$	Ferrobielastic	Mechanically second order	$\sigma\sigma$
...	...	...	...	...

$i, j = 1, 2, 3$; $\mu, \nu = 1, 2, \ldots, 6$.

Table 3.4.3.2. *Four types of domain pairs*

F_{1j}	J_{1j}	K_{1j}	Double coset	Domain pair name	symbol
$F_1 = F_j$	$F_1 \cup g^\star_{1j} F_1$	$F_1 \cup g^\star_{1j} F_1$	$F_1 g_{1j} F_1 = g_{1j} F_1 = (g_{1j} F_1)^{-1}$	transposable completely	tc
$F_{1j} \subset F_1$	$F_{1j} \cup g^\star_{1j} F_{1j}$	$F_1 \cup g^\star_{1j} F_1 \cup \ldots$	$F_1 g_{1j} F_1 = (F_1 g_{1j} F_1)^{-1}$	transposable partially	tp
$F_1 = F_j$	F_1	$F_1 \cup g_{1j} F_1 \cup g_{1j}^{-1} F_1$	$F_1 g_{1j} F_1 = g_{1j} F_1 \cap (g_{1j} F_1)^{-1} = \emptyset$	non-transposable simple	ns
$F_{1j} \subset F_1$	F_{1j}	$F_1 \cup g_{1j} F_1 \cup (g_{1j} F_1)^{-1} \cup \ldots$	$F_1 g_{1j} F_1 \cap (F_1 g_{1j} F_1)^{-1} = \emptyset$	non-transposable multiple	nm

(Wadhawan, 2000). We consider in our classification always the potential ferroelectric (ferroelastic) phase.

A closer look at equation (3.4.3.33) reveals a correspondence between the difference coefficients in front of products of field components and the tensor distinction of domain states $\mathbf{S}_1$ and $\mathbf{S}_j$ in the domain pair $(\mathbf{S}_1, \mathbf{S}_j)$: If a morphic Cartesian tensor component of a *polar* tensor is different in these two domain states, then the corresponding difference coefficient is nonzero and defines components of fields that can switch one of these domain states into the other. A similar statement holds for the symmetric tensors of rank two (*e.g.* the spontaneous strain tensor).

Tensor distinction for all representative non-ferroelastic domain pairs is available in the synoptic Table 3.4.3.4. These data also carry information about the switching fields.

3.4.3.4. *Classes of equivalent domain pairs and their classifications*

Two domain pairs that are crystallographically equivalent, $(\mathbf{S}_i, \mathbf{S}_k) \overset{G}{\sim} (\mathbf{S}_l, \mathbf{S}_m)$ [see equation (3.4.3.5)], have different orientations in space but their inherent properties are the same. It is, therefore, useful to divide all domain pairs of a ferroic phase into classes of equivalent domain pairs. All domain pairs that are equivalent (in G) with a given domain pair, say $(\mathbf{S}_i, \mathbf{S}_k)$, can be obtained by applying to $(\mathbf{S}_i, \mathbf{S}_k)$ all operations of G, *i.e.* by forming a G-orbit $G(\mathbf{S}_i, \mathbf{S}_k)$.

One can always find in this orbit a domain pair $(\mathbf{S}_1, \mathbf{S}_j)$ that has in the first place the first domain state $\mathbf{S}_1$. We shall call such a pair a *representative domain pair of the orbit*. The initial orbit $G(\mathbf{S}_i, \mathbf{S}_k)$ and the orbit $G(\mathbf{S}_1, \mathbf{S}_j)$ are identical:

$$G(\mathbf{S}_i, \mathbf{S}_k) = G(\mathbf{S}_1, \mathbf{S}_j).$$

The set P of n^2 ordered pairs (including trivial ones) that can be formed from n domain states can be divided into G-orbits (classes of equivalent domain pairs):

$$\mathsf{P} = G(\mathbf{S}_1, \mathbf{S}_1) \cup G(\mathbf{S}_1, g_2\mathbf{S}_1) \cup \ldots \cup (\mathbf{S}_1, g_j\mathbf{S}_1) \cup \ldots \cup G(\mathbf{S}_1, g_q\mathbf{S}_1). \quad (3.4.3.34)$$

Similarly, as there is a one-to-one correspondence between domain states and left cosets of the stabilizer (symmetry group) F_1 of the first domain state [see equation (3.4.2.9)], there is an analogous relation between G-orbits of domain pairs and so-called double cosets of F_1.

A *double coset* $F_1 g_j F_1$ *of* F_1 is a set of left cosets that can be expressed as fg_jF_1, where $f \in F_1$ runs over all operations of F_1 (see Section 3.2.3.2.8). A group G can be decomposed into disjoint double cosets of $F_1 \subset G$:

$$G = F_1 e F_1 \cup F_1 g_2 F_1 \cup \ldots \cup F_1 g_j F_1 \cup \ldots \cup F_1 g_q F_1, \quad j = 1, 2, \ldots, q, \quad (3.4.3.35)$$

where $g_1 = e, g_2, \ldots g_j, \ldots g_q$ is the set of representatives of double cosets.

There is a one-to-one correspondence between double cosets of the decomposition (3.4.3.35) and G-orbits of domain pairs (3.4.3.34) (see Section 3.2.3.3.6, Proposition 3.2.3.35):

$$G(\mathbf{S}_1, \mathbf{S}_j) \leftrightarrow F_1 g_j F_1, \quad \text{where} \quad \mathbf{S}_j = g_j\mathbf{S}_1, \quad j = 1, 2, \ldots, q. \quad (3.4.3.36)$$

We see that the representatives g_j of the double cosets in decomposition (3.4.3.35) define domain pairs $(\mathbf{S}_1, g_j\mathbf{S}_1)$ which represent all different G-orbits of domain pairs. Just as different left cosets g_iF_1 specify all domain states, different double cosets determine all classes of equivalent domain pairs (G-orbits of domain pairs).

The properties of double cosets are reflected in the properties of corresponding domain pairs and provide a natural classification of domain pairs. A specific property of a double coset is that it is either identical or disjoint with its inverse. A double coset that is identical with its inverse,

$$(F_1 g_j F_1)^{-1} = F_1 g_j^{-1} F_1 = F_1 g_j F_1, \quad (3.4.3.37)$$

is called an *invertible (ambivalent) double coset*. The corresponding class of domain pairs consists of transposable (ambivalent) domain pairs.

A double coset that is disjoint with its inverse,

$$(F_1 g_j F_1)^{-1} = F_1 g_j^{-1} F_1 \cap F_1 g_j F_1 = \emptyset, \quad (3.4.3.38)$$

is a *non-invertible (polar) double coset* (∅ denotes an empty set) and the corresponding class of domain pairs comprises non-transposable (polar) domain pairs. A double coset $F_1 g_j F_1$ and its inverse $(F_1 g_j F_1)^{-1}$ are called *complementary double cosets*. Corresponding classes called *complementary classes of equivalent domain pairs* consist of transposed domain pairs that are non-equivalent.

Another attribute of a double coset is the number of left cosets which it comprises. If an invertible double coset consists of one left coset,

$$F_1 g_j F_1 = g_j F_1 = (g_j F_1)^{-1}, \quad (3.4.3.39)$$

then the domain pairs in the G-orbit $G(\mathbf{S}_1, g_j\mathbf{S}_1)$ are completely transposable. An invertible double coset comprising several left cosets is associated with a G-orbit consisting of partially transposable domain pairs. Non-invertible double cosets can be divided into simple non-transposable double cosets (complementary double cosets consist of one left coset each) and multiple non-transposable double cosets (complementary double cosets comprise more than one left coset each).

Thus there are four types of double cosets (see Table 3.2.3.1 in Section 3.2.3.2) to which there correspond the four basic types of domain pairs presented in Table 3.4.3.2.

These results can be illustrated using the example of a phase transition with $G = 4_z/m_zm_xm_{xy} \supset 2_xm_ym_z = F_1$ with four domain states (see Fig. 3.4.2.2). The corresponding four left cosets of $2_xm_ym_z$ are given in Table 3.4.2.1. Any operation from the first left coset (identical with F_1) transforms the second left coset into itself, *i.e.* this left coset is a double coset. Since it consists of an operation of order two, it is a simple invertible double coset. The corresponding representative domain pair is $(\mathbf{S}_1, \bar{1}\mathbf{S}_1) = (\mathbf{S}_1, \mathbf{S}_2)$. By applying operations of $G = 4_z/m_zm_xm_{xy}$ on $(\mathbf{S}_1, \mathbf{S}_2)$, one gets the class of equivalent domain pairs (G-orbit): $(\mathbf{S}_1, \mathbf{S}_2) \overset{G}{\sim} (\mathbf{S}_2, \mathbf{S}_1) \overset{G}{\sim} (\mathbf{S}_3, \mathbf{S}_4) \overset{G}{\sim} (\mathbf{S}_4, \mathbf{S}_3)$. These domain pairs can be labelled as '180° pairs' according to the angle between the spontaneous polarization in the two domain states.

When one applies operations from the first left coset on the third left coset, one gets the fourth left coset, therefore a double coset consists of these two left cosets. An inverse of any operation

references