

3.4. DOMAIN STRUCTURES

$$S_{jk} = h_j p_k S_{11}, \quad S_{11} = S_1, \quad j = 1, 2, \dots, n_\lambda, \quad k = 1, 2, \dots, d_\lambda, \quad (3.4.2.24)$$

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 transitions involving a spontaneous distortion of the crystal lattice that entails a change of shape of the crystallographic or conventional unit cell (Wadhawan, 2000). Such a transformation is accompanied by a change in the number of independent nonzero components of a symmetric second-rank tensor u that describes spontaneous strain.

In discussing ferroelastic and non-ferroelastic domain structures, the concepts of crystal family and holohedry of a point group are useful (IT A, 2005). Crystallographic point groups (and space groups as well) can be divided into seven crystal systems and six *crystal families* (see Table 3.4.2.2). A symmetry descent within a crystal family does not entail a qualitative change of the spontaneous strain – the number of independent nonzero tensor components of the strain tensor u remains unchanged.

We shall call the largest group of the crystal family to which the group M belongs the *family group of M* (symbol FamM). Then a simple criterion for a ferroic phase transition with symmetry descent $G \subset F$ to be a *non-ferroelastic phase transition* is

$$F \subset G, \quad \text{Fam}F = \text{Fam}G. \quad (3.4.2.25)$$

A necessary and sufficient condition for a *ferroelastic phase transition* is

$$F \subset G, \quad \text{Fam}F \neq \text{Fam}G. \quad (3.4.2.26)$$

A *ferroelastic domain state* R_i is defined as a state with a homogeneous spontaneous strain $u^{(i)}$. [We drop the suffix ‘s’ or ‘(s)’ if the serial number of the domain state is given as the superscript (i). The definition of spontaneous strain is given in Section 3.4.3.6.1.] Different ferroelastic domain states differ in spontaneous strain. The symmetry of a ferroelastic domain state R_i is specified by the stabilizer $I_G(u^{(i)})$ of the spontaneous strain $u^{(i)}$ of the principal domain state S_i [see (3.4.2.16)]. This stabilizer, which we shall denote by A_i , can be expressed as an intersection of the parent group G and the family group of F_i (see Table 3.4.2.2):

$$A_i \equiv I_G(u^{(i)}) = G \cap \text{Fam}F_i. \quad (3.4.2.27)$$

This equation indicates that the ferroelastic domain state R_i has a prominent single-domain orientation. Further on, the term ‘ferroelastic domain state’ will mean a ‘ferroelastic domain state in single-domain orientation’.

In our illustrative example,

$$\begin{aligned} A_1 &= I_{4_z/m_z m_x m_{xy}}(u_{11} - u_{22}) \\ &= \text{Fam}(2_x m_y m_z) \cap m 4_z / m_z m_x m_{xy} \\ &= m_x m_y m_z \cap 4_z / m_z m_x m_{xy} = m_x m_y m_z. \end{aligned}$$

The number n_a of ferroelastic domain states is given by

$$n_a = [G : A_1] = |G| : |A_1|. \quad (3.4.2.28)$$

In our example, $n_a = |4_z/m_z m_x m_{xy}| : |m_x m_y m_z| = 16 : 8 = 2$. In Table 3.4.2.7, last column, the number n_a of ferroelastic domain states is given for all possible ferroic phase transitions.

The number d_a of principal domain states compatible with one ferroelastic domain state (degeneracy of ferroelastic domain states) is given by

$$d_a = [A_1 : F_1] = |A_1| : |F_1|. \quad (3.4.2.29)$$

In our example, $d_a = |m_x m_y m_z| : |2_x m_y m_z| = 8 : 4 = 2$, i.e. two non-ferroelastic principal domain states are compatible with each of the two ferroelastic domain states (cf. Fig. 3.4.2.2).

The product of n_a and d_a is equal to the number n of all principal domain states [see equation (3.4.2.19)],

$$n_a d_a = [G : A_1][A_1 : F_1] = [G : F_1] = n. \quad (3.4.2.30)$$

The number d_a of principal domain states in one ferroelastic domain state can be calculated for all ferroic phase transitions from the ratio of numbers n and n_a that are given in Table 3.4.2.7.

According to Aizu (1969), we can recognize three possible cases (see also Table 3.4.2.3):

(i) *Full ferroelastics*: All principal domain states differ in spontaneous strain. In this case, $n_a = n$, i.e. $A_1 = F_1$, ferroelastic domain states are identical with principal domain states.

(ii) *Partial ferroelastics*: Some but not all principal domain states differ in spontaneous strain. A necessary and sufficient condition is $1 < n_a < n$, or, equivalently, $F_1 \subset A_1 \subset G$. In this case, ferroelastic domain states are degenerate secondary domain states with degeneracy $n > d_a = |A_1| : |F_1| > 1$. In this case, the phase transition $G \supset F_1$ can also be classified as an *improper ferroelastic* one (see Section 3.1.3.2).

(iii) *Non-ferroelastics*: All principal domain states have the same spontaneous strain. The criterion is $n_a = 1$, i.e. $A_1 = G$.

Example 3.4.2.1. Domain states in leucite. Leucite (KAlSi₂O₆) (see e.g. Hatch *et al.*, 1990) undergoes at about 938 K a ferroelastic phase transition from cubic symmetry $G = m\bar{3}m$ to tetragonal symmetry $L = 4/mmm$. This phase can appear in $|m\bar{3}m| : |4/mmm| = 3$ single-domain states, which we denote R_1, R_2, R_3 . The symmetry group of the first domain state R_1 is

Table 3.4.2.2. Crystal systems, holohedries, crystal families and number of spontaneous strain components

Point group M	Crystal system	Holohedry HolM	Spontaneous strain components		Crystal family	Family group FamM
			Independent	Nonzero		
23, $m\bar{3}$, 432, $\bar{4}3m$, $m\bar{3}m$	Cubic	$m\bar{3}m$	1	3	Cubic	$m\bar{3}m$
6, $\bar{6}$, 6/m, 622, 6mm, $\bar{6}2m$, 6/mmmm	Hexagonal	6/mmm	2	3	Hexagonal	6/mmm
3, $\bar{3}$, 32, 3m, $\bar{3}m$	Trigonal	$\bar{3}m$	2	3		
4, $\bar{4}$, 4/m, 422, 4mm, $\bar{4}2m$, 4/mmm	Tetragonal	4/mmm	2	3	Tetragonal	4/mmm
222, mm2, mmm	Orthorhombic	mmm	3	3	Orthorhombic	mmm
2, m, 2/m	Monoclinic	2/m	4	4	Monoclinic	2/m
1, $\bar{1}$	Triclinic	$\bar{1}$	6	6	Triclinic	$\bar{1}$

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Table 3.4.2.3. Classification of ferroic phases according to ferroelastic and ferroelectric domain states

n_e , n_a and n : number of ferroelectric, ferroelastic and principal domain states, respectively. Terms in parentheses were introduced by Aizu (1970a).

Ferroelastic			Ferroelectric			
$n_a = n$	$1 < n_a < n$	$n_a = 1$	$n_e = n$	$1 < n_e < n$	$n_e = 1$	$n_e = 0$
faithful (full)	degenerate (partial)	non-ferroelastic (non-ferroelastic)	faithful (full)	degenerate (partial)	trivial	zero
f or af	d or ad	n or an	f or ef	d or ed	t or et	z or ez
					non-ferroelectric (non-ferroelectric)	
					n or en	

$L_1 = 4_x/m_x m_y m_z$. This group equals the stabilizer $I_G(u^{(1)})$ of the spontaneous strain $u^{(1)}$ of \mathbf{R}_1 since $\text{Fam}(4_x/m_x m_y m_z) = 4_x/m_x m_y m_z$ (see Table 3.4.2.2), hence this phase is a full ferroelastic one.

At about 903 K, another phase transition reduces the symmetry $4/mmm$ to $F = 4/m$. Let us suppose that this transition has taken place in a domain state \mathbf{R}_1 with symmetry $L_1 = 4_x/m_x m_y m_z$; then the room-temperature ferroic phase has symmetry $F_1 = 4_x/m_x$. The $4_x/m_x m_y m_z \supset 4_x/m_x$ phase transition is a non-ferroelastic one [$\text{Fam}(4_x/m_x) = 4_x/m_x m_y m_z$] with $|4_x/m_x m_y m_z| : |4_x/m_x| = 8 : 4 = 2$ non-ferroelastic domain states, which we denote \mathbf{S}_1 and \mathbf{S}_2 . Similar considerations performed with initial domain states \mathbf{R}_2 and \mathbf{R}_3 generate another two couples of principal domain states $\mathbf{S}_3, \mathbf{S}_4$ and $\mathbf{S}_5, \mathbf{S}_6$, respectively. Thus the room-temperature phase is a partially ferroelastic phase with three degenerate ferroelastic domain states, each of which can contain two principal domain states. Both ferroelastic domains and non-ferroelastic domains within each ferroelastic domain have been observed [see Fig. 3.3.10.13 in Chapter 3.3, Palmer *et al.* (1988) and Putnis (1992)].

3.4.2.2.2. Ferroelectric domain states

Ferroelectric domain states are defined as states with a homogeneous spontaneous polarization; different ferroelectric domain states differ in the direction of the spontaneous polarization. Ferroelectric domain states are specified by the stabilizer $I_G(\mathbf{P}_s^{(1)})$ of the spontaneous polarization $\mathbf{P}_s^{(1)}$ in the first principal domain state \mathbf{S}_1 [see equation (3.4.2.16)]:

$$F_1 \subseteq C_1 \equiv I_G(\mathbf{P}_s^{(1)}) \subseteq G. \quad (3.4.2.31)$$

The stabilizer C_1 is one of ten polar groups: 1, 2, 3, 4, 6, m , $mm2$, $3m$, $4mm$, $6mm$. Since F_1 must be a polar group too, it is simple to find the stabilizer C_1 fulfilling relation (3.4.2.31).

The number n_e of ferroelectric domain states is given by

$$n_e = [G : C_1] = |G| : |C_1|. \quad (3.4.2.32)$$

If the polar group C_1 does not exist, we put $n_e = 0$. The number n_e of ferroelectric domain states is given for all ferroic phase transitions in the eighth column of Table 3.4.2.7.

The number d_a of principal domain states compatible with one ferroelectric domain state (degeneracy of ferroelectric domain states) is given by

$$d_e = [C_1 : F_1] = |C_1| : |F_1|. \quad (3.4.2.33)$$

The product of n_e and d_e is equal to the number n of all principal domain states [see equation (3.4.2.19)],

$$n_e d_e = n. \quad (3.4.2.34)$$

The degeneracy d_e of ferroelectric domain states can be calculated for all ferroic phase transitions from the ratio of the numbers n and n_e that are given in Table 3.4.2.7.

Aizu (1969, 1970a) recognizes three possible cases (see also Table 3.4.2.3):

(i) *Full ferroelectrics*: All principal domain states differ in spontaneous polarization. In this case, $n_e = n$, *i.e.* $C_1 = F_1$, ferroelectric domain states are identical with principal domain states.

(ii) *Partial ferroelectrics*: Some but not all principal domain states differ in spontaneous polarization. A necessary and sufficient condition is $1 < n_e < n$, or equivalently, $F_1 \subset C_1 \subset G$. Ferroelectric domain states are degenerate secondary domain states with degeneracy $n > d_e > 1$. In this case, the phase transition $G \supset F_1$ can be classified as an *improper ferroelectric* one (see Section 3.1.3.2).

(iii) *Non-ferroelectrics*: No principal domain states differ in spontaneous polarization. There are two possible cases: (a) The parent phase is polar; then $C_1 = G$ and $n_e = 1$. (b) The parent phase is non-polar; in this case a polar stabilizer C_1 does not exist, then we put $n_e = 0$.

The classification of full-, partial- and non-ferroelectrics and ferroelastics is summarized in Table 3.4.2.3.

Results for all symmetry descents follow readily from the numbers n , n_a , n_e in Table 3.4.2.7 and are given for all symmetry descents in Aizu (1970a). One can conclude that partial ferroelectrics are rather rare.

Example 3.4.2.3. Domain structure in tetragonal perovskites. Some perovskites (*e.g.* barium titanate, BaTiO_3) undergo a phase transition from the cubic parent phase with $G = m\bar{3}m$ to a tetragonal ferroelectric phase with symmetry $F_1 = 4_x m_y m_z$. The stabilizer $A_1 = \text{Fam}(4_x m_y m_z) \cap m\bar{3}m = 4_x/m_x m_y m_z$. There are $n_a = |m\bar{3}m| : |4_x/m_x m_y m_z| = 3$ ferroelastic domain states each compatible with $d_a = |4_x/m_x m_y m_z| : |4_x m_y m_z| = 2$ principal ferroelectric domain states that are related *e.g.* by inversion $\bar{1}$, *i.e.* spontaneous polarization is antiparallel in two principal domain states within one ferroelastic domain state.

A similar situation, *i.e.* two non-ferroelastic domain states with antiparallel spontaneous polarization compatible with one ferroelastic domain state, occurs in perovskites in the trigonal ferroic phase with symmetry $F = 3m$ and in the orthorhombic ferroic phase with symmetry $F_1 = m_{xy} 2_{xy} m_z$.

Many other examples are discussed by Newnham (1974, 1975), Newnham & Cross (1974a,b), and Newnham & Skinner (1976).

3.4.2.2.3. Domain states with the same stabilizer

In our illustrative example (see Fig. 3.4.2.2), we have seen that two domain states \mathbf{S}_1 and \mathbf{S}_2 have the same symmetry group (stabilizer) $2_x m_y m_z$. In general, the condition 'to have the same stabilizer (symmetry group)' divides the set of n principal domain states into equivalence classes. As shown in Section 3.2.3.3, the role of an intermediate group L_1 is played in this case by the normalizer $N_G(F_1)$ of the symmetry group F_1 of the first domain state \mathbf{S}_1 . The number d_F of domain states with the same symmetry group is given by [see Example 3.2.3.34 in Section 3.2.3.3.5 and equation (3.2.3.95)],