

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

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
<b>f</b> or <b>af</b>	<b>d</b> or <b>ad</b>	<b>n</b> or <b>an</b>	<b>f</b> or <b>ef</b>	<b>d</b> or <b>ed</b>	<b>t</b> or <b>et</b>	<b>z</b> or <b>ez</b>
					non-ferroelectric (non-ferroelectric)	
					<b>n</b> or <b>en</b>	

$L_1 = 4_x/m_x m_y m_z$ . 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,  $\text{BaTiO}_3$ ) 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)],

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$$d_F = [N_G(F_1) : F_1] = |N_G(F_1)| : |F_1|. \quad (3.4.2.35)$$

The number  $n_F$  of subgroups that are conjugate under  $G$  to  $F_1$  can be calculated from the formula [see equation (3.2.3.96)]

$$n_F = [G : N_G(F_1)] = |G| : |N_G(F_1)|. \quad (3.4.2.36)$$

The product of  $n_F$  and  $d_F$  is equal to the number  $n$  of ferroic domain states,

$$n = n_F d_F. \quad (3.4.2.37)$$

The normalizer  $N_G(F_1)$  enables one not only to determine which domain states have the symmetry  $F_1$  but also to calculate all subgroups that are conjugate under  $G$  to  $F_1$  (see Examples 3.2.3.22, 3.2.3.29 and 3.2.3.34 in Section 3.2.3.3).

Normalizers  $N_G(F_1)$  and the number  $d_F$  of principal domain states with the same symmetry are given in Table 3.4.2.7 for all symmetry descents  $G \supset F_1$ . The number  $n_F$  of subgroups conjugate to  $F_1$  is given by  $n_F = n : d_F$ .

All these results obtained for point-group symmetry descents can be easily generalized to microscopic domain states and space-group symmetry descents (see Section 3.4.2.5).

#### 3.4.2.3. Property tensors associated with ferroic domain states

In the preceding section we derived relations for domain states without considering their specific physical properties. Basic formulae for the number of principal and secondary domain states [see equations (3.4.2.11) and (3.4.2.17), respectively] and the transformation properties of these domain states [equations (3.4.2.12) and (3.4.2.21), respectively] follow immediately from the symmetry groups  $G$ ,  $F_1$  of the parent and ferroic phases, respectively. Now we shall examine which components of property tensors specify principal and secondary domain states and how these tensor components change in different domain states.

A property tensor  $\tau$  is specified by its components. The number  $m_i(\tau)$  of independent tensor components of a certain tensor  $\tau$  depends on the point-group symmetry  $G$  of the crystal (see Chapter 1.1). The number  $m_c(\tau)$  of nonzero Cartesian (rectangular) components depends on the orientation of the crystal in the reference Cartesian coordinate system and is equal to, or greater than, the number  $m_i(\tau)$  of independent tensor components; this number  $m_i(\tau)$  is independent of orientation. Then there are  $m_c(\tau) - m_i(\tau)$  linear relations between Cartesian tensor components. The difference  $m_c(\tau) - m_i(\tau)$  is minimal for a 'standard' orientation, in which symmetry axes of the crystal are, if possible, parallel to the axes of the reference coordinate system [for more on this choice, see Nye (1985) Appendix B, Sirotnin & Shaskolskaya (1982), Shuvalov (1988) and *IEEE Standards on Piezoelectricity* (1987)]. Even in this standard orientation, only for point groups of triclinic, monoclinic and orthorhombic crystal systems is the number  $m_c(\tau)$  of nonzero Cartesian components of each property tensor equal to the number  $m_i(\tau)$  of independent tensor components, *i.e.* all Cartesian tensor components are independent. For all other point groups  $m_c(\tau) - m_i(\tau) > 0$ , *i.e.* there are always relations between some Cartesian tensor components. One can verify this statement for the strain tensor in Table 3.4.2.2.

The relations between Cartesian tensor components can be removed when one uses *covariant tensor components*. [Kopský (1979); see also the manual of the the software *GI★KoBo-1* and Kopský (2001). An analogous decomposition of Cartesian tensors into irreducible parts has been performed by Jerphagnon *et al.* (1978).] Covariant tensor components are linear combinations of Cartesian tensor components that transform according to irreducible matrix representations  $D^{(\omega)}(G)$  of the group  $G$  of the crystal (*i.e.* they form a basis of irreducible representations of  $G$ ; see Chapter 1.2). The number of covariant tensor

components equals the number of independent components of the tensor  $\tau$ .

The advantage of expressing property tensors by covariant tensor components becomes obvious when one considers a change of a property tensor at a ferroic phase transition. A symmetry descent  $G \supset F_1$  is accompanied by the preservation of, or an increase of, the number of independent Cartesian tensor components. The latter possibility can manifest itself either by the appearance of morphic Cartesian tensor components in the low-symmetry phase or by such changes of nonzero Cartesian components that break some relations between tensor components in the high-symmetry phase. This is seen in our illustrative example of the strain tensor  $u$ . In the high-symmetry phase with  $G = 4_2/m_z m_x m_{xy}$ , the strain tensor has two independent components and three nonzero components:  $u_{11} \neq u_{22} = u_{33}$ . In the low-symmetry phase with  $F_1 = 2_x m_y m_z$ , there are three independent and three nonzero components:  $u_{11} \neq u_{22} \neq u_{33}$ , *i.e.* the equation  $u_{22} = u_{33}$  does not hold in the parent phase. This change cannot be expressed by a single Cartesian morphic component.

Since there are no relations between covariant tensor components, any change of tensor components at a symmetry descent can be expressed by morphic covariant tensor components, which are zero in the parent phase and nonzero in the ferroic phase. In our example, the covariant tensor component of the spontaneous strain is  $u_{11} - u_{22}$ , which is a morphic component since  $u_{11} - u_{22} = 0$  for the symmetry  $4_2/m_z m_x m_{xy}$  but  $u_{11} - u_{22} \neq 0$  for symmetry  $2_x m_y m_z$ .

Tensorial covariants are defined in an exact way in the manual of the software *GI★KoBo-1* and in Kopský (2001). Here we give only a brief account of this notion. Consider a crystal with symmetry  $G$  and a property tensor  $\tau$  with  $n_\tau$  independent tensor components. Let  $D^{(\omega)}(G)$  be a  $d_\alpha$ -dimensional physically irreducible matrix representation of  $G$ . The  $D^{(\omega)}(G)$  *covariant* of  $\tau$  consists of the following  $d_\alpha$  *covariant tensor components*:  $\tau_a^\alpha = (\tau_{a,1}^\alpha, \tau_{a,2}^\alpha, \dots, \tau_{a,d_\alpha}^\alpha)$ , where  $a = 1, 2, \dots$  and  $m = n_\tau/d_\alpha$  numbers different  $d_\alpha$ -tuples formed from  $n_\tau$  components of  $\tau$ . These covariant tensor components are linear combinations of Cartesian components of  $\tau$  that transform as so-called typical variables of the matrix representation  $D^{(\omega)}(G)$ , *i.e.* the transformation properties under operations  $g \in G$  of covariant tensor components are expressed by matrices  $D^{(\omega)}(g)$ .

The relation between two presentations of the tensor  $\tau$  is provided by *conversion equations*, which express Cartesian tensor components as linear combinations of covariant tensor components and *vice versa* [for details see the manual and Appendix E of the software *GI★KoBo-1* and Kopský (2001)].

Tensorial covariants for all non-equivalent physically irreducible matrix representations of crystallographic point groups and all important property tensors up to rank four are listed in the software *GI★KoBo-1* and in Kopský (2001). Thus, for example, in Table D of the software *GI★KoBo-1*, or in Kopský (2001) p. 5, one finds for the two-dimensional irreducible representation  $E$  of group 422 the following tensorial covariants:  $(P_1, P_2)$ ,  $(d_{11}, d_{22})$ ,  $(d_{12}, d_{21})$ ,  $(d_{13}, d_{23})$ ,  $(d_{26}, d_{16})$ ,  $(d_{35}, d_{34})$ .

Let us denote by  $\tau_a^{(\omega)(1)}$  a tensorial covariant of  $\tau$  in the first single-domain state  $\mathbf{S}_1$ . A crucial role in the analysis is played by the stabilizer  $I_G(\tau_a^{(\omega)(1)})$  of these covariants, *i.e.* all operations of the parent group  $G$  that leave  $\tau_a^{(\omega)(1)}$  invariant. There are three possible cases:

(1) If

$$I_G(\tau_a^{(\omega)(1)}) = G, \quad (3.4.2.38)$$

then all components of  $\tau_a^{(\omega)(1)}$  that are nonzero in the parent phase are also nonzero in the ferroic phase. All these components are the same in all principal domain states. For important property tensors and for all point groups  $G$ , these covariant tensor components are listed in the main tables of the software