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

differs in hexagonal and trigonal crystals from the crystallographic coordinate system common in crystallography. Last but not least, a ready-to-use and user-friendly presentation calls for symbols that are explicit and concise.

To meet these requirements, we use in this chapter, in Section 3.1.3 and in the software *GI⋆KoBo*-1 a symbolism in which the orientations of crystallographic elements and operations are expressed by means of suffixes related to a reference Cartesian coordinate system. The relation of this reference Cartesian coordinate system – called a *crystallophysical coordinate system* – to the usual crystallographic coordinate system is a matter of convention. We adhere to the generally accepted rules [see Nye (1985) Appendix B, Sirotin & Shaskolskaya (1982), Shuvalov (1988), and *IEEE Standards on Piezoelectricity*, 1987].

We list all symbols of crystallographic symmetry operations and a comparison of these symbols with other notations in Tables 3.4.2.5 and 3.4.2.6 and in Figs. 3.4.2.3 and 3.4.2.4.

Now we can present the synoptic Table 3.4.2.7.

3.4.2.4.1. *Explanation of Table 3.4.2.7*

G: point group expressing the *symmetry of the parent (prototypic) phase*. Subscripts of generators in the group symbol specify their orientation in the Cartesian (rectangular) crystallophysical coordinate system of the group G (see Tables 3.4.2.5 and 3.4.2.6, and Figs. 3.4.2.3 and 3.4.2.4).

F_1: this point group is a proper subgroup of G given in the first column and expresses the *symmetry of the ferroic phase in the first single-domain state* $\mathbf{S}_1$. In accordance with *IT* A (2005), five groups are given in two orientations (bold and normal type). Subscripts of generators in the group symbol specify their orientation in the Cartesian (rectangular) crystallophysical coordinate system of the group G (see Tables 3.4.2.5 and 3.4.2.6, and Figs. 3.4.2.3and 3.4.2.4). In the cubic groups, the direction of the body diagonal is denoted by abbreviated symbols: $p \equiv [111]$ (all *positive*), $q \equiv [\bar{1}11]$, $r \equiv [1\bar{1}1]$, $s \equiv [11\bar{1}]$. In the hexagonal and trigonal groups, axes x', y' and x'', y'' of a Cartesian coordinate system are rotated about the z axis through 120 and 240°, respectively, from the crystallophysical Cartesian coordinate axes x and y.

Symmetry groups in parentheses are groups conjugate to F_1 under G (see Section 3.2.3.2). These are symmetry groups (stabilizers) of some domain states $\mathbf{S}_k$ different from $\mathbf{S}_1$ (for more details see Section 3.4.2.2.3).

Γ_η: *physically irreducible representation of the group G*. This specifies the transformation properties of the principal tensor parameter of the phase transition in a continuum description and transformation properties of the primary order parameter η
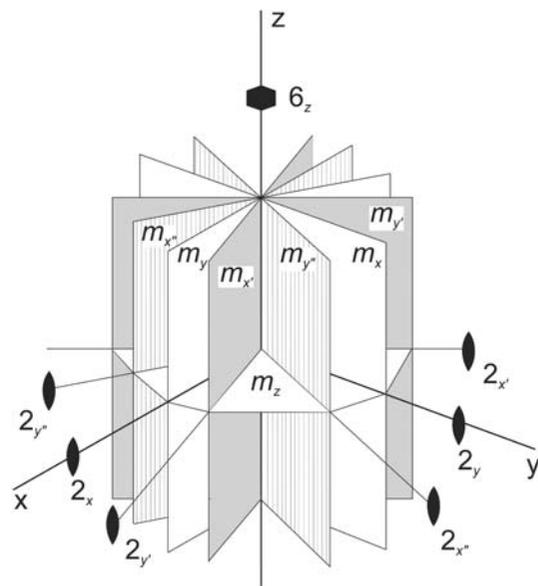

Fig. 3.4.2.4. Oriented symmetry operations of the hexagonal group $6/mmm$ and of its hexagonal and trigonal subgroups. The coordinate system x, y, z corresponds to the Cartesian crystallophysical coordinate system, the axes x, y, z of the crystallographic coordinate system are parallel to the twofold rotation axes $2_x, 2_{x'}$ and to the sixfold rotation axis 6_z. Correlation with other notations is given in Table 3.4.2.6.

of the *equitranslational* phase transitions in the microscopic description. The letters A, B signify one-dimensional representations, and letters E and T two- and three-dimensional irreducible representations, respectively. Two letters T indicate that the symmetry descent $G \subset F_1$ can be accomplished by two non-equivalent three-dimensional irreducible representations (see Table 3.1.3.2). 'Reducible' denotes a reducible representation of G. In this case, there are always several non-equivalent reducible representations inducing the same descent $G \subset F_1$ [for more detailed information see the software *GI⋆KoBo*-1 and Kopský (2001)].

Knowledge of Γ_η enables one to determine for all ferroic transitions property tensors and their components that are different in all principal domain states, and, for equitranslational transitions only, microscopic displacements and/or ordering of atoms and molecules that are different in different basic (microscopic) domain states (for details see Section 3.1.3, especially Table 3.1.3.1, and Section 3.1.2).

$N_G(F_1)$: the *normalizer of* F_1 *in* G (defined in Section 3.2.3.2.4) determines subgroups conjugate to F_1 in G and specifies which

Table 3.4.2.6. *Symbols of symmetry operations of the point group 6/mmm*

Standard: symbols used in Section 3.1.3, in the present chapter and in the software; suffixes (in italic) refer to the Cartesian crystallophysical coordinate system. BC: Bradley & Cracknell (1972). AH: Altmann & Herzig (1994). *IT* A: *IT* A (2005), coordinates (in Sans Serif) are expressed in a crystallographic hexagonal basis. Jones: Jones' faithful representation symbols express the action of a symmetry operation of a vector (xyz) in a crystallographic basis (see *e.g.* Bradley & Cracknell, 1972).

Standard	BC	AH	*IT* A	Jones	Standard	BC	AH	*IT* A	Jones
1 or e	E	E	1	x, y, z	$\bar{1}$ or i	I	I	$\bar{1}$ 0, 0, 0	$\bar{x}, \bar{y}, \bar{z}$
6_z	C_6^+	C_6^+	6^+ 0, 0, z	$x-y, x, z$	$\bar{6}_z$	S_3^-	S_3^-	$\bar{6}^+$ 0, 0, z	$y-x, \bar{x}, \bar{z}$
3_z	C_3^+	C_3^+	3^+ 0, 0, z	$\bar{y}, x-y, z$	$\bar{3}_z$	S_6^-	S_6^-	$\bar{3}^+$ 0, 0, z	$y, y-x, \bar{z}$
2_z	C_2	C_2	2 0, 0, z	$\bar{x}, \bar{y}, z$	m_z	σ_h	σ_h	m x, y, 0	$x, y, \bar{z}$
3_z^2	C_3^-	C_3^-	3^- 0, 0, z	$y-x, \bar{x}, z$	$\bar{3}_z^5$	S_6^+	S_6^+	$\bar{3}^-$ 0, 0, z	$x-y, x, \bar{z}$
6_z^5	C_6^-	C_6^-	6^- 0, 0, z	$y, y-x, z$	$\bar{6}_z^5$	S_3^+	S_3^+	$\bar{6}^-$ 0, 0, z	$\bar{y}, x-y, \bar{z}$
2_x	C_{21}''	C_{21}''	2 x, 0, 0	$x-y, \bar{y}, \bar{z}$	m_x	σ_{v1}	σ_{v1}	m x, 2x, z	$y-x, y, z$
$2_{x'}$	C_{22}''	C_{22}''	2 0, y, 0	$\bar{x}, y-x, \bar{z}$	$m_{x'}$	σ_{v2}	σ_{v2}	m 2x, x, z	$x, x-y, z$
$2_{x''}$	C_{23}''	C_{23}''	2 x, x, 0	$y, x, \bar{z}$	$m_{x''}$	σ_{v3}	σ_{v3}	m x, $\bar{x}$, z	$\bar{y}, \bar{x}, z$
2_y	C_{21}'	C_{21}'	2 x, 2x, 0	$y-x, y, \bar{z}$	m_y	σ_{d1}	σ_{d1}	m x, 0, z	$x-y, \bar{y}, z$
$2_{y'}$	C_{22}'	C_{22}'	2 2x, x, 0	$x, x-y, \bar{z}$	$m_{y'}$	σ_{d2}	σ_{d2}	m 0, y, z	$\bar{x}, y-x, z$
$2_{y''}$	C_{23}'	C_{23}'	2 x, $\bar{x}$, 0	$\bar{y}, \bar{x}, \bar{z}$	$m_{y''}$	σ_{d3}	σ_{d3}	m x, x, z	y, x, z

domain states have the same symmetry (stabilizer in G). The number n_F of subgroups conjugate to F_1 in G is $n_F = [G : N_G(F_1)] = |G| : |N_G(F_1)|$ [see equation (3.4.2.36)] and the number d_F of principal domain states with the same symmetry is $d_F = [N_G(F_1) : F_1] = |N_G(F_1)| : |F_1|$ [see equation (3.4.2.35)]. There are three possible cases:

(i) $N_G(F_1) = G$. There are no subgroups conjugate to F_1 and the symmetry group F_i (stabilizer of $\mathbf{S}_i$ in G) of all principal domain states $\mathbf{S}_1, \mathbf{S}_2, \ldots, \mathbf{S}_n$ is equal to F_i for all $i = 1, 2, \ldots, n$; hence domain states cannot be distinguished by their symmetry. The group F_1 is a normal subgroup of G, $F_1 \triangleleft G$ (see Section 3.2.3.2). This is always the case if there are just two single-domain states $\mathbf{S}_1$, $\mathbf{S}_2$, i.e. if the index of F_1 in G equals two, $[G : F_1] = |G| : |F_1| = 2$.

(ii) $N_G(F_1) = F_1$. Then any two domain states $\mathbf{S}_i$, $\mathbf{S}_k$ have different symmetry groups (stabilizers), $\mathbf{S}_i \neq \mathbf{S}_k \Leftrightarrow F_i \neq F_k$, i.e. there is a one-to-one correspondence between single-domain states and their symmetries, $\mathbf{S}_i \Leftrightarrow F_i$. In this case, principal domain states $\mathbf{S}_i$ can be specified by their symmetries F_i, $i = 1, 2, \ldots, n$. The number n_F of different groups conjugate to F_1 is equal to the index $[G : F_1] = |G| : |F_1| = n$.

(iii) $F_1 \subset N_G(F_1) \subset G$. Some, but not all, domain states $\mathbf{S}_i$, $\mathbf{S}_k$ have identical symmetry groups (stabilizers) $F_i = F_k$. The number d_F of domain states with the same symmetry group is $d_F = [N_G(F_1) : F_1] = |N_G(F_1)| : |F_1|$ [see equation (3.4.2.35)], $1 < d_F < n$. The number n_F of different groups conjugate to F_1 is equal to the index $n_F = [G : N_G(F_1)] = |G| : |N_G(F_1)|$ [see equation (3.4.2.36)] and in this case $1 < n_F < n$. It always holds that $n_F d_F = n$ [see equation (3.4.2.37)].

$K_G(F_1, g_{1j})$: twinning group of a domain pair $(\mathbf{S}_1, \mathbf{S}_j)$. This group is defined in Section 3.4.3.2. It can be considered a colour (polychromatic) group involving c colours, where $c = [K_{1j} : F_1]$, and is, therefore, defined by two groups K_{1j} and F_1, and its full symbol is $K_{1j}(F_1)$. In this column only K_{1j} is given, since F_1 appears in the second column of the table.

If the group symbol of K_{1j} contains generators with the star symbol, $\star$, which signifies transposing operations of the domain pair $(\mathbf{S}_1, \mathbf{S}_j)$, then the symbol $K_{1j}(F_1)$ denotes a dichromatic ('black-and-white') group signifying a completely transposable domain pair. In this special case, just the symbol K_{1j} containing stars $\star$ specifies the group F_1 unequivocally.

The number in parentheses after the group symbol of K_{1j} is equal to the number of twinning groups K_{1k} equivalent with K_{1j}.

In the continuum description, a twinning group is significant in at least in two instances:

(1) A twinning group $K_{1j}(F_1)$ specifies the distinction of two domain states $\mathbf{S}_1$ and $\mathbf{S}_j = g_{1j}\mathbf{S}_1$, where $g_{1j} \in G$ (see Sections 3.4.3.2 and 3.4.3.4).

(2) A twinning group $K_{1j}(F_1)$ may assist in signifying classes of equivalent domain pairs (orbits of domain pairs). In most cases, to a twinning group F_{1j} there corresponds just one class of equivalent domain pairs (an orbit) $G(\mathbf{S}_1, \mathbf{S}_j)$; then a twinning group can represent this class of equivalent domain pairs. Nevertheless, in some cases two or more classes of equivalent domain pairs have a common twinning group. Then one has to add a switching operation g_{1j} to the twinning group, $K_{1j}(F_1, g_{1j})$ (see the end of Section 3.4.3.2). In this way, classes of equivalent domain pairs $G(\mathbf{S}_1, \mathbf{S}_j)$ are denoted in synoptic Tables 3.4.2.7 and 3.4.3.6.

Twinning groups given in column K_{1j} thus specify all G-orbits of domain pairs. The number of G-orbits and representative domain pairs for each orbit are determined by double cosets of group F_1 (see Section 3.4.3.2). Representative domain pairs from each orbit of domain pairs are further analysed in synoptic Table 3.4.3.4 (non-ferroelastic domain pairs) and in synoptic Table 3.4.3.6 (ferroelastic domain pairs).

The set of the twinning groups K_{1j} given in this column is analogous to the concept of a complete twin defined as 'an edifice comprising in addition to an original crystal (domain state $\mathbf{S}_1$) as many twinned crystals (domain states $\mathbf{S}_j$) as there are possible twin laws' (see Curien & Le Corre, 1958). If a traditional definition of a twin law ['a geometrical relationship between two crystal components of a twin', see Section 3.3.2 and Koch (2004); Curien & Le Corre (1958)] is applied sensu stricto to domain twins then one gets the following correspondence:

(i) a twin law of a non-ferroelastic domain twin is specified by the twinning group K_{1j} (see Section 3.4.3.3 and Table 3.4.3.4);

(ii) two twin laws of two compatible ferroelastic domain twins, resulting from one ferroelastic single-domain pair $\{\mathbf{S}_1, \mathbf{S}_j\}$, are specified by two layer groups $\bar{J}_{1j}$ associated with the twinning group K_{1j} of this ferroelastic single-domain pair $\{(\mathbf{S}_1, \mathbf{S}_j)\}$ (see Section 3.4.3.4 and Table 3.4.3.6).

n: number of principal single-domain states, the finest subdivision of domain states in a continuum description, $n = [G : F_1] = |G| : |F_1|$ [see equation (3.4.2.11)].

d_F: number of principal domain states with the same symmetry group (stabilizer), $d_F = [N_G(F_1) : F_1] = |N_G(F_1)| : |F_1|$ [see equation (3.4.2.35)]. If $d_F > 1$, then the group F_1 does not specify the first single-domain state $\mathbf{S}_1$. The number n_F of subgroups conjugate with F_1 is $n_F = n : d_F$.

n_e: number of ferroelectric single-domain states, $n_e = [G : C_1] = |G| : |C_1|$, where C_1 is the stabilizer (in G) of the spontaneous polarization in the first domain state $\mathbf{S}_1$ [see equation (3.4.2.32)]. The number d_e of principal domain states compatible with one ferroelectric domain state (degeneracy of ferroelectric domain states) equals $d_e = [C_1 : F_1] = |C_1| : |F_1|$ [see equation (3.4.2.33)].

Aizu's classification of ferroelectric phases (Aizu, 1969; see Table 3.4.2.3): $n_e = n$, fully ferroelectric; $1 < n_e < n$, partially ferroelectric; $n_e = 1$, non-ferroelectric, the parent phase is polar and the spontaneous polarization in the ferroic phase is the same as in the parent phase; $n_e = 0$, non-ferroelectric, parent phase is non-polar.

n_a: number of ferroelastic single-domain states, $n_a = [G : A_1] = |G| : |A_1|$, where A_1 is the stabilizer (in G) of the spontaneous strain in the first domain state $\mathbf{S}_1$ [see equation (3.4.2.28)]. The number d_a of principal domain states compatible with one ferroelastic domain state (degeneracy of ferroelastic domain states) is given by $d_a = [A_1 : F_1] = |A_1| : |F_1|$ [see equation (3.4.2.29)].

Aizu's classification of ferroelastic phases (Aizu, 1969; see Table 3.4.2.3): $n_a = n$, fully ferroelastic; $1 < n_a < n$, partially ferroelastic; $n_e = 1$, non-ferroelastic.

Example 3.4.2.5. Orthorhombic phase of perovskite crystals. The parent phase has symmetry $G = m\bar{3}m$ and the symmetry of the ferroic orthorhombic phase is $F_1 = m_{x\bar{y}}2_{xy}m_z$. In Table 3.4.2.7, we find that $n = n_e$, i.e. the phase is fully ferroelectric. Then we can associate with each principal domain state a spontaneous polarization. In column K_{1j} there are four twinning groups. As explained in Section 3.4.3, these groups represent four 'twin laws' that can be characterized by the angle between the spontaneous polarization in single-domain state $\mathbf{S}_1$ and $\mathbf{S}_j$, $j = 2, 3, 4, 5$. If we choose $\mathbf{P}_{(s)}^{(1)}$ along the direction [110] (F_1 does not specify unambiguously this direction, since $d_F = 2$!), then the angles between $\mathbf{P}_{(s)}^{(1)}$ and $\mathbf{P}_{(s)}^{(j)}$, representing the 'twin law' for these four twinning groups $m\bar{3}m(m_{zx})$, $m\bar{3}m(2_{zx})$, $4_z/m_z m_x m_{xy}$, $m_{x\bar{y}}m_{xy}^{\star}m_z$, are, respectively, 60, 120, 90 and 180°.

3.4.2.5. Basic (microscopic) domain states and their partition into translation subsets

The examination of principal domain states performed in the continuum approach can be easily generalized to a microscopic description. Let us denote the space-group symmetry of the parent (high-symmetry) phase by $\mathcal{G}$ and the space group of the

references