

## 3.4. DOMAIN STRUCTURES

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

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 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

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

*GI★KoBo-1* and in Kopský (2001). The corresponding Cartesian tensor components are available in Section 1.1.4 and in standard textbooks (e.g. Nye, 1985; Sirotnin & Shaskolskaya, 1982).

(2) If

$$I_G(\tau_a^{(\omega(1))}) = F_1, \quad (3.4.2.39)$$

then any of  $m = n_\tau/d_\alpha$  tensorial covariants  $\tau_a^{(\omega)}$ ,  $a = 1, 2, \dots, m$ , is a possible principal tensor parameter  $\varphi^{(1)}$  of the transition  $G \supset F_1$ . Any two of  $n_f = |G| : |F_1|$  principal domain states differ in some, or all, components of these covariants. The principal tensor parameter  $\varphi$  plays a similar symmetric (but generally not thermodynamic) role as the order parameter  $\eta$  does in the Landau theory. Only for equitranslational phase transitions is one of the principal tensor parameters (that with the temperature-dependent coefficient) identical with the primary order parameter of the Landau theory (see Section 3.1.3).

(3) If

$$I_G(\tau_a^{(\omega(1))}) = L_1, \quad F_1 \subset L_1 \subset G, \quad (3.4.2.40)$$

then  $\tau_a^{(\omega(1))}$  represents the secondary tensor parameter  $\lambda$  (see Section 3.1.3.2). There exist  $n_\lambda = |G| : |L_1|$  secondary domain states  $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{n_\lambda}$  that differ in  $\lambda$ . Unlike in the two preceding cases (1) and (2), several intermediate groups  $L_1, M_2, \dots$  (with secondary tensor parameters  $\lambda, \mu, \dots$ ) that fulfil condition (3.4.2.40) can exist.

Now we shall indicate how one can find particular property tensors that fulfil conditions (3.4.2.39) or (3.4.2.40). The solution of this group-theoretical task consists of three steps:

(i) For a given point-group symmetry descent  $G \supset F_1$ , or  $G \supset L_1$ , one finds the *representation*  $\Gamma_\eta$  that specifies the *transformation properties of the principal, or secondary, tensor parameter*, which plays the role of the order parameters in a continuum description. This task is called an inverse Landau problem (see Section 3.1.3 for more details). The solution of this problem is available in Tables 3.4.2.7 and 3.1.3.1, in the software *GI★KoBo-1* and in Kopský (2001), where the letters  $A, B$  signify one-dimensional irreducible representations, and letters  $E$  and  $T$  two- and three-dimensional ones. The dimensionality  $d_\eta$ , or  $d_\lambda$ , of the representation  $\Gamma_\eta$ , or  $\Gamma_\lambda$ , specifies the maximal number of independent components of the principal, or secondary, tensor parameter  $\varphi$ , or  $\lambda$ , respectively. ‘Reducible’ indicates that  $\Gamma_\eta$  is a reducible representation.

(ii) In Table 3.1.3.1 one finds in the second column, for a given  $G$  and  $\Gamma_\eta$ , or  $\Gamma_\lambda$  (first column), the *standard variables* designating in a standardized way the covariant tensor components of the principal, or secondary, tensor parameters (for more details see Section 3.1.3.1 and the manual of the software *GI★KoBo-1*). For two- and three-dimensional irreducible representations, this column contains relations that restrict the values of the components and thus reduce the number of independent components.

(iii) *The association of covariant tensor components* of property tensors *with standard variables* is tabulated for all irreducible representations in an abridged version in Table 3.1.3.1, in the

column headed *Principal tensor parameters*, and in full in the main table of the software *GI★KoBo-1* and of Kopský (2001).

Phase transitions associated with reducible representations are treated in detail only in the software *GI★KoBo-1* and in Kopský (2001). Fortunately, these phase transitions occur rarely in nature.

A rich variety of observed structural phase transitions can be found in Tomaszewski (1992). This database lists 3446 phase transitions in 2242 crystalline materials.

*Example 3.4.2.4. Morphic tensor components associated with  $4_z/m_z m_x m_{xy} \supset 2_x m_y m_z$  symmetry descent*

(1) *Principal tensor parameters*  $\varphi^{(1)}$ . The representation  $\Gamma_\eta$  that specifies the transformation properties of the principal tensor parameter  $\varphi^{(1)}$  (and for equitranslational phase transitions also the primary order parameter  $\eta^{(1)}$ ) can be found in the first column of Table 3.1.3.1 for  $G = 4_z/m_z m_x m_{xy}$  and  $F_1 = 2_x m_y m_z$ ; the  $R$ -irreducible representation ( $R$ -irep)  $\Gamma_\eta = E_u$ . Therefore, the principal tensor parameter  $\varphi^{(1)}$  (or the primary order parameter  $\eta^{(1)}$ ) has two components  $(\varphi_1^{(1)}, \varphi_2^{(1)})$  [or  $(\eta_1^{(1)}, \eta_2^{(1)})$ ]. The standard variables are in the second column:  $(x_1^-, 0)$ . This means that only the first component  $\varphi_1^{(1)}$  (or  $\eta_1^{(1)}$ ) is nonzero. In the column *Principal tensor parameters*, one finds that  $\varphi_1^{(1)} = P_1$  (or  $\eta_1^{(1)} = P_1$ ), i.e. one principal tensor parameter is spontaneous polarization and the spontaneous polarization in the first domain state  $\mathbf{S}_1$  is  $P_{(s)} = (P, 00)$ . Other principal tensor parameters can be found in the software *GI★KoBo-1* or in Kopský (2001), p. 185:  $(g_4, 0)$ ,  $(d_{11}, 0)$ ,  $(d_{12}, 0)$ ,  $(d_{13}, 0)$ ,  $(d_{26}, 0)$ ,  $(d_{35}, 0)$  (the physical meaning of the components is explained in Table 3.4.3.5).

(2) *Secondary tensor parameters*  $\lambda^{(1)}, \mu^{(1)}, \dots$

In the group lattice (group–subgroup chains) in Fig. 3.1.3.1, one finds that the only intermediate group between  $4_z/m_z m_x m_{xy}$  and  $2_x m_y m_z$  is  $L_1 = m_x m_y m_z$ . In the same table of the software *GI★KoBo-1* or in Kopský (2001), one finds  $\Gamma_\lambda = B_{1g}$  and the following one-dimensional secondary tensor parameters:  $u_1 - u_2$ ;  $A_{14} + A_{25}$ ,  $A_{36}$ ;  $s_{11} - s_{22}$ ,  $s_{13} - s_{23}$ ,  $s_{44} - s_{55}$ ;  $Q_{11} - Q_{22}$ ,  $Q_{12} - Q_{21}$ ,  $Q_{13} - Q_{23}$ ,  $Q_{31} - Q_{32}$ ,  $Q_{44} - Q_{55}$ .

The use of covariant tensor components has two practical advantages:

Firstly, the change of tensor components at a ferroic phase transition is completely described by the appearance of new nonzero covariant tensor components. If needed, Cartesian tensor components corresponding to covariant components can be calculated by means of *conversion equations*, which express Cartesian tensor components as linear combinations of covariant tensor components [for details on tensor covariants and conversion equations see the manual and Appendix E of the software *GI★KoBo-1* and Kopský (2001)].

Secondly, calculation of property tensors in various domain states is substantially simplified: transformations of Cartesian tensor components, which are rather involved for higher-rank tensors, are replaced by a simpler transformation of covariant tensor components by matrices  $D^{(n)}$  of the matrix representation of  $\Gamma_\eta$ , or of  $\Gamma_\lambda$  [see again the software *GI★KoBo-1* and Kopský

Table 3.4.2.4. *Morphic properties, tensor parameters, order parameters and domain states*

T, U, S, V: property tensors; TOP: designation of tensor or order parameter;  $\Gamma$ : representation of  $G$  expressing the transformation properties of TOP. The terms ‘full’ and ‘partial’ were introduced by Aizu (1970a).

Morphic property	TOP	$\Gamma$	Stabilizer of TOP	Domain states
Spontaneous components of tensor T	$\varphi$	$\Gamma_\varphi$	$F_1$	Principal (full) in tensor T
Spontaneous components of tensor U	$\psi$	$\Gamma_\psi$	$F_1$	Principal (full) in tensor U
Spontaneous components of tensor S	$\sigma$	$\Gamma_\sigma$	$F_1$	Principal (full) in tensor S
Spontaneous components of tensor V	$\lambda$	$\Gamma_\lambda$	$L_1, F_1 \subset L_1 \subset G$	Degenerate (partial) in tensor V
Primary order parameter	$\eta$	$\Gamma_\eta$	$\mathcal{F}_1$	Basic (microscopic)
Pseudoproper order parameter	$\zeta$	$\Gamma_\eta$	$\mathcal{F}_1$	Basic (microscopic)
Secondary (improper) order parameter	$\xi$	$\Gamma_\xi$	$\mathcal{L}_1, \mathcal{F}_1 \subset \mathcal{L}_1 \subset \mathcal{G}$	Secondary (improper) microscopic

