

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

provided by the *conversion equations* that express Cartesian tensor components as linear combinations of principal and secondary covariant components (for more details on tensorial covariants and conversion equations see Appendix E of the manual for *GI★KoBo-1* and Kopský, 2001).

We illustrate the situation on a transition with symmetry descent  $4_2 2_x 2_{xy} \Downarrow 2_x 2_y 2_z$ . In Table 3.1.3.1, we find that the principal tensor parameter transforms according to irreducible representation  $B_1$  with standard variable  $x_3$ . The corresponding covariant  $u_3 = u_1 - u_2$  can be found in Appendix E of the manual of *GI★KoBo-1* (or in Kopský, 2001), where one also finds an invariant containing  $u_1$  and  $u_2$ :  $u_{1,1} = u_1 + u_2$ . The corresponding conversion equations are:  $u_1 = \frac{1}{2}(u_{1,1} + u_3)$ ,  $u_2 = \frac{1}{2}(u_{1,1} - u_3)$ . In the parent phase  $u_3 = u_1^{(p)} - u_2^{(p)} = 0$ , hence  $u_1^{(p)} = u_2^{(p)} = \frac{1}{2}u_{1,1}$ , whereas in the ferroic phase  $u_1^{(f)} = \frac{1}{2}(u_{1,1} + u_3) = u_1^{(p)} + \frac{1}{2}u_3 = u_1^{(p)} + \delta u_1$ ,  $u_2^{(f)} = u_2^{(p)} - \frac{1}{2}u_3 = u_2^{(p)} - \delta u_2 = u_1^{(p)} - \delta u_1$ . The symmetry-breaking increments  $\delta u_1 = -\delta u_2$  describe thus the changes of the Cartesian components that correspond to the nonzero principal tensor component  $u_1 - u_2$ .

An analogous situation occurs frequently in trigonal and hexagonal parent groups, where  $u_1 - u_2$  (or  $g_1 - g_2$ ) transforms like the first or second component of the principal tensor parameter. In these cases, the corresponding symmetry-breaking increments of Cartesian components are again related:  $\delta u_1 = -\delta u_2$  (or  $\delta g_1 = -\delta g_2$ ).

We note that relations like  $A_{11} = -A_{12} = -A_{26}$  do not imply that these components transform as the standard variable. Though these components are proportional to the principal tensor parameter in the first domain state, they cannot be transformed to corresponding components in other domain states as easily as covariant tensor components of the principal tensor parameter.

In general, it is useful to consider a tensor parameter as a vector in the carrier space of the respective representation. Then the Cartesian components are projections of this vector on the Cartesian basis of the tensor space.

The presentation of the principal tensor parameters in the column *Principal tensor parameters* of this table is a compromise: whenever conversion equations lead to simple relations between morphic Cartesian components and/or symmetry-breaking increments, we present these relations, in some cases together with corresponding covariants. In the more complicated cases, only the covariants are given. The corresponding conversion equations and labelling of covariants are given at the beginning of that part of the table which covers hexagonal and cubic parent groups  $G$ . In the main tables of the software *GI★KoBo-1*, the principal tensor parameters and the secondary tensor parameters up to rank 4 are given consistently in covariant form. Labelling of covariant components and conversion equations are given in Appendix E of the manual.

The principal tensor parameters presented in Table 3.1.3.1 represent a particular choice of property tensors for standard variables given in the second column. To save space, property tensors are selected in the following way: polarization  $\mathbf{P}$  and strain  $u$  are always listed; if none of their components transform according to  $D^{(n)}$ , then components of one axial and one polar tensor (if available) appearing in Table 3.1.3.3 are given. Principal parameters of two different property tensors are separated by a semicolon. If two different components of the same property tensor transform in the same way, they are separated by a comma.

As tensor indices we use integers 1, 2, 3 instead of vector components  $x, y, z$  and contracted indices 1, 2, 3, 4, 5, 6 in matrix notation for pairs  $xx, yy, zz, yz \approx zy, zx \approx xz, xy \approx yx$ , respectively

*Important note:* To make Table 3.1.3.1 compatible with the software *GI★KoBo-1* and with Kopský (2001), coefficients of property tensors in matrix notation with contracted indices 4, 5, 6 do not contain the numerical factors 2 and 4 which are usually

Table 3.1.3.3. *Important property tensors*

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

Tensor components	Property	Tensor components	Property
$\varepsilon$	enantiomorphism		chirality
$P_i$	polarization	$P_i$	pyroelectricity
$u_\mu$	strain	$\varepsilon_{ij}$	dielectric permittivity
$g_\mu$	optical activity		
$d_{i\mu}$	piezoelectricity	$r_{i\mu}$	electro-optics
$A_{i\mu}$	electrogyration		
$\pi_{\mu\nu}$	piezo-optics	$Q_{\mu\nu}$	electrostriction

introduced to preserve a compact form (without these factors) of linear constitutive relations [see Chapter 1.1, Nye (1985) and especially Appendices E and F of Sirotin & Shaskolskaya (1982)]. This explains the differences in matrix coefficients appearing in Table 3.1.3.1 and those presented in Chapter 1.1 or in Nye (1985) and in Sirotin & Shaskolskaya (1982). Thus *e.g.* for the symmetry descent  $6_z 2_x 2_y \Downarrow 3_z 2_x$ , we find in Table 3.1.3.1 the principal tensor parameters  $d_{11} = -d_{12} = -d_{26}$ , whereas according to Chapter 1.1 or *e.g.* to Nye (1985) or Sirotin & Shaskolskaya (1982) these coefficients for  $F_1 = 3_z 2_x$  are related by equations  $d_{11} = -d_{12} = -2d_{26}$ .

Property tensors and symbols of their components that can be found in Table 3.1.3.1 are given in the left-hand half of Table 3.1.3.3. The right-hand half presents other tensors that transform in the same way as those on the left and form, therefore, covariant tensor components of the same form as those given in the column *Principal tensor parameters*. Principal and secondary tensor parameters for all property tensors that appear in Table 3.1.3.3 are available in the software *GI★KoBo-1*.

$n_f$ : number of ferroic single domain states that differ in the primary order parameter  $\eta$  and in the principal tensor parameters.

$n_a$ : number of ferroelastic single domain states. If  $n_a = n_f$ ,  $n_a < n_f$  or  $n_a = 1$ , the ferroic phase is, respectively, a full, partial or non-ferroelastic one.

$n_e$ : number of ferroelectric single domain states. If  $n_e = n_f$ ,  $n_e < n_f$  or  $n_e = 0, 1$ , the ferroic phase is, respectively, a full, partial or non-ferroelectric one ( $n = 0$  or  $n = 1$  correspond to a non-polar or to a polar parent phase, respectively) (see Section 3.4.2).

3.1.3.4. *Examples*

*Example 3.1.3.4.1. Phase transition in triglycine sulfate (TGS).* Assume that the space groups of both parent (high-symmetry) and ferroic (low-symmetry) phases are known:  $\mathcal{G} = P2_1/c (C_{2h}^5)$ ,  $\mathcal{F}_1 = P2_1 (C_2^2)$ . The same number of formula units in the primitive unit cell in both phases suggests that the transition is an equitranslational one. This conclusion can be checked in the lattice of equitranslational subgroups of the software *GI★KoBo-1*. There we find for the low-symmetry space group the symbol  $P112_1(\mathbf{b}/4)$ , where the vector in parentheses expresses the shift of the origin with respect to the conventional origin given in *IT A* (2005).

In Table 3.1.3.1, one finds that the corresponding point-group-symmetry descent  $2_z/m_z \Downarrow 2_z$  is associated with irreducible representation  $\Gamma_\eta = A_u$ . The corresponding principal tensor parameters of lowest rank are the pseudoscalar  $\varepsilon$  (enantiomorphism or chirality) and the vector of spontaneous polarization with one nonzero morphic component  $P_3$  – the transition is a proper ferroelectric one. The non-ferroelastic ( $n_a = 1$ ) full ferroelectric phase has two ferroelectric domain states ( $n_f = n_e = 2$ ). Other principal tensor parameters (morphic tensor components that transform according to  $\Gamma_\eta$ ) are available in the software *GI★KoBo-1*:  $g_1, g_2, g_3, g_6; d_{31}, d_{32}, d_{33}, d_{36}, d_{14}, d_{15}, d_{24}, d_{25}$ . Property tensors with these components are listed in Table 3.1.3.3. As shown in Section 3.4.2, all these components

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change sign when one passes from one domain state to the other. Since there is no intermediate group between  $G$  and  $F$ , there are no secondary tensor parameters.

*Example 3.1.3.4.2. Phase transitions in barium titanate ( $BaTiO_3$ ).* We shall illustrate the solution of the inverse Landau problem and the need to correlate the crystallographic system with the Cartesian crystallophysical coordinate system. The space-group type of the parent phase is  $\mathcal{G} = Pm\bar{3}m$ , and those of the three ferroic phases are  $\mathcal{F}_1^{(1)} = P4mm$ ,  $\mathcal{F}_1^{(2)} = Cm2m$ ,  $\mathcal{F}_1^{(3)} = R3m$ , all with one formula unit in the primitive unit cell.

This information is not complete. To perform mode analysis, we must specify these space groups by saying that the lattice symbol  $P$  in the first case and the lattice symbol  $R$  in the third case are given with reference to the cubic crystallographic basis ( $\mathbf{a}, \mathbf{b}, \mathbf{c}$ ), while lattice symbol  $C$  in the second case is given with reference to crystallographic basis  $[(\mathbf{a} - \mathbf{b}), (\mathbf{a} + \mathbf{b}), \mathbf{c}]$ . If we now identify vectors of the cubic crystallographic basis with vectors of the Cartesian basis by  $\mathbf{a} = ae_x$ ,  $\mathbf{b} = ae_y$ ,  $\mathbf{c} = ae_z$ , where  $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$  are three orthonormal vectors, we can see that the corresponding point groups are  $F_1^{(1)} = 4_z m_x m_y$ ,  $F_1^{(2)} = m_{xy} 2_{xy} m_z$ ,  $F_1^{(3)} = 3_p m_{xy}$ .

Notice that without specification of crystallographic bases one could interpret the point group of the space group  $Cm2m$  as  $m_x 2_y m_z$ . Bases are therefore always specified in lattices of equitranslational subgroups of the space groups that are available in the software *GI★KoBo-1*, where we can check that all three symmetry descents are equitranslational.

In Table 3.1.3.1, we find that these three ferroic subgroups are epikernels of the  $R$ -irep  $\Gamma_\eta = T_{1u}$  with the following principal tensor components:  $P_3$ ,  $P_1 = P_2$ ,  $P_1 = P_2 = P_3$ , respectively. Other principal tensor parameters can be found in the main tables of the software *GI★KoBo-1*. The knowledge of the representation  $\Gamma_\eta$  allows one to perform soft-mode analysis (see e.g. Rousseau *et al.*, 1981).

For the tetragonal ferroelectric phase with  $F_1 = 4_z m_x m_y$ , we find in Fig. 3.1.3.1 an intermediate group  $L_1 = 4_z/m_z m_x m_y$ . In Table 3.1.3.1, we check that this is an epikernel of the  $R$ -irep  $E_g$  with secondary tensor parameter  $\delta u_3$ . This phase is a full (proper) ferroelectric and partial ferroelastic one.

More details about symmetry aspects of structural phase transitions can be found in monographs by Izyumov & Syromiatnikov (1990), Kociński (1983, 1990), Landau & Lifshitz (1969), Lyubarskii (1960), Tolédano & Dmitriev (1996) and Tolédano & Tolédano (1987). Group-subgroup relations of space groups are treated extensively in *IT A1* (2004).

#### 3.1.4. Example of a table for non-equitranslational phase transitions

BY J.-C. TOLÉDANO

In the preceding Section 3.1.3, a systematic tabulation of possible symmetry changes was provided for the class of equitranslational phase transitions. This tabulation derives from the principles described in Section 3.1.2, and relates the enumeration of the symmetry changes at structural transitions to the characteristics of the irreducible representations of the space group  $\mathcal{G}$  of the ‘parent’ (highest-symmetry) phase adjacent to the transition. Systematic extension of this type of tabulation to the general case of transitions involving both a decrease of translational and of point-group symmetry has been achieved by several groups (Tolédano & Tolédano, 1976, 1977, 1980, 1982; Stokes & Hatch, 1988). The reader can refer, in particular, to the latter reference for an exhaustive enumeration of the characteristics of possible transitions. An illustration of the results obtained for a restricted class of parent phases (those associated with the point symmetry  $4/m$  and to a simple Bravais lattice  $P$ ) is presented here.

In order to clarify the content Table 3.1.4.1, let us recall (*cf.* Section 3.1.2) that Landau’s theory of continuous phase transitions shows that the order parameter of a transition transforms according to a physically irreducible representation of the space group  $\mathcal{G}$  of the high-symmetry phase of the crystal. A physically irreducible representation is either a real irreducible representation of  $\mathcal{G}$  or the direct sum of two complex-conjugate irreducible representations of  $\mathcal{G}$ . To classify the order-parameter symmetries of all possible transitions taking place between a given parent (high-symmetry) phase and another (low-symmetry) phase, it is therefore necessary, for each parent space group, to list the various relevant irreducible representations.

Each irreducible representation of a given space group can be denoted  $\Gamma_n(k^*)$  and identified by two quantities. The star  $k^*$ , represented by a vector linking the origin of reciprocal space to a point of the first Brillouin zone, specifies the translational symmetry properties of the basis functions of  $\Gamma_n(k^*)$ . The dimension of  $\Gamma_n(k^*)$  is equal to the number of components of the order parameter of the phase transition considered. A given space group has an infinite number of irreducible representations. However, physical considerations restrict a systematic enumeration to only a few irreducible representations. The restrictions arise from the fact that one focuses on continuous (or almost continuous) transitions between strictly periodic crystal structures (*i.e.* in particular, incommensurate phases are not considered), and have been thoroughly described previously (Tolédano & Tolédano, 1987, and references therein).

#### 3.1.5. Microscopic aspects of structural phase transitions and soft modes

BY J. F. SCOTT

##### 3.1.5.1. Introduction

Phase transitions in crystals are most sensitively detected *via* dynamic techniques. Two good examples are ultrasonic attenuation and internal friction. Unfortunately, while often exquisitely sensitive to subtle second-order phase transitions [*e.g.* the work of Spencer *et al.* (1970) on  $BaMnF_4$ ], they provide no real structural information on the lattice distortions that occur at such phase transitions, or even convincing evidence that a real phase transition has occurred (*e.g.* transition from one long-range thermodynamically stable ordered state to another). It is not unusual for ultrasonic attenuation to reveal a dozen reproducible anomalies over a small temperature range, none of which might be a phase transition in the usual sense of the phrase. At the other extreme are detailed structural analyses *via* X-ray or neutron scattering, which give unambiguous lattice details but often totally miss small, nearly continuous rigid rotations of light ions, such as hydrogen bonds or oxygen or fluorine octahedra or tetrahedra. Intermediate between these techniques are phonon spectroscopies, notably infrared (absorption or reflection) and Raman techniques. The latter has developed remarkably over the past thirty years since the introduction of lasers and is now a standard analytical tool for helping to elucidate crystal structures and phase transitions investigated by chemists, solid-state physicists and materials scientists.

##### 3.1.5.2. Displacive phase transitions

###### 3.1.5.2.1. Landau–Devonshire theory

Landau (1937) developed a simple mean-field theory of phase transitions which implicitly assumes that each atom or ion in a system exerts a force on the other particles that is independent of the distance between them (see Section 3.1.2.2). Although this is a somewhat unphysical crude approximation to the actual forces, which are strongly dependent upon interparticle spacings, it allows the forces of all the other particles in the system to be replaced mathematically by an effective ‘field’, and for the