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 (**a**, **b**, **c**), while lattice symbol C in the second case is given with reference to crystallographic basis [(**a** − **b**), (**a** + **b**), **c**]. If we now identify vectors of the cubic crystallographic basis with vectors of the Cartesian basis by $\mathbf{a} = a\mathbf{e}_x$, $\mathbf{b} = a\mathbf{e}_y$, $\mathbf{c} = a\mathbf{e}_z$, where $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ are three orthonormal vectors, we can see that the corresponding point groups are $F_1^{(1)} = 4_z m_x m_{xy}$, $F_1^{(2)} = m_{x\bar{y}} 2_{xy} m_z$, $F_1^{(3)} = 3_p m_{x\bar{y}}$.

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 Γ_η 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 $L_1 = 4_z/m_z m_x m_{xy}$. In Table 3.1.3.1, we check that this is an epikernel of the R-irep E_g with secondary tensor parameter δu_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 (2003).

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 quantifies. 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