

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

resulting equations to be solved exactly. This mathematical simplicity preserves the qualitative features of the real physical system and its phase transition without adding unnecessary cumbersome mathematics and had earlier been used to great advantage for fluids by Van der Waals (1873) and for magnetism by Weiss (1907). Landau's theory is a kind of generalization of those earlier theories. In it he defines an 'order parameter' x , in terms of which most physical quantities of interest may be expressed *via* free energies. In a ferromagnet, the order parameter corresponds to the net magnetization; it is zero above the Curie temperature T_c and increases monotonically with decreasing temperature below that temperature. In a liquid-gas phase transition the order parameter is the difference in density in the gas and liquid phases for the fluid.

Devonshire independently developed an equivalent theory for ferroelectric crystals around 1953 (Devonshire, 1954). For ferroelectrics, the order parameter is the spontaneous dielectric polarization P . In both his formalism and that of Landau, the ideas are most conveniently expressed through the free energy of the thermodynamic system:

$$F(P, T) = A(T - T_c)P^2 + BP^4 + CP^6, \quad (3.1.5.1a)$$

where A and C are positive quantities and B may have either sign. Scott (1999) shows that C changes sign at ferroelectric-to-

superionic conducting transition temperatures. As shown in Fig. 3.1.5.1, minimization of the free energy causes the expectation value of P to go from zero above the Curie temperature to a nonzero value below. If B is positive the transition is continuous ('second-order'), whereas if B is negative, the transition is discontinuous ('first-order'), as shown in Fig. 3.1.5.2. The coefficient B may also be a function of pressure p or applied electric field \mathbf{E} and may pass through zero at a critical threshold value of p or \mathbf{E} . Such a point is referred to as a 'tricritical point' and is marked by a change in the order of the transition from first-order to second-order. The term 'tri-critical' originates from the fact that in a three-dimensional graph with coordinates temperature T , pressure p and applied field \mathbf{E} , there are *three* lines marking the ferroelectric-paraelectric phase boundary that meet at a single point. Crossing any of these three lines produces a continuous phase transition (Fig. 3.1.5.3).

3.1.5.2.2. Soft modes

Minimization of the free energy above leads to the dependence of spontaneous polarization P upon temperature given by $P(T) = P(0)[(T_c - T)/T_c]$ for continuous transitions. In the more general case discussed by Landau, the polarization P is replaced by a generic 'order parameter' $\varphi(T)$ with the same dependence. Cochran's contribution (1960, 1961) was to show that for

Table 3.1.4.1. Possible symmetry changes across transitions from a parent phase with space group $P4/m$, $P4_2/m$, $P4/n$, $P4_2/n$, $I4/m$ or $I4_1/a$

Equitranslational symmetry changes are not included (*cf.* Section 3.1.3). The coordinates of the points in the second column are referred to the primitive unit cell of the reciprocal lattice. The terms used in the fifth column are introduced in Section 3.1.1. The last column is characteristic of non-equitranslational transitions.

Parent space group	Irreducible representation		Possible low-symmetry space groups	Macroscopic characteristics of the transition	Change in the number of atoms per primitive unit cell
	Brillouin zone point	Dimension of the order parameter			
$P4/m$	$\frac{1}{2}, \frac{1}{2}, 0$	2	$P2/m; P2/b$	Ferroelastic	2
		1	$P4/m; P4/n$	Non-ferroic	2
	$0, 0, \frac{1}{2}$	2	$P2_1/m$	Ferroelastic	2
		1	$P4/m; P4_2/m$	Non-ferroic	2
	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	2	$B2/m$	Ferroelastic	2
		1	$I4/m$	Non-ferroic	2
	$0, \frac{1}{2}, \frac{1}{2}$	2	$B2/m$	Ferroelastic	2
		1	$I4/m$	Non-ferroic	4
	$0, \frac{1}{2}, 0$	2	$P2/m; P2/b$	Ferroelastic	2
		1	$P4/m; P4/n$	Non-ferroic	4
$P4_2/m$	$\frac{1}{2}, \frac{1}{2}, 0$	2	$P2/m; P2/b$	Ferroelastic	2
		1	$P4_2/n; P4_2/m$	Non-ferroic	2
	$0, 0, \frac{1}{2}$	2	$P2_1/m$	Ferroelastic	2
		2	$P4_1; P4_3$	Ferroelectric	2
	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	2	$B2/m$	Ferroelastic	2
		1	$I4/m$	Non-ferroic	2
	$0, \frac{1}{2}, \frac{1}{2}$	2	$B2/m$	Ferroelastic	2
		2	$P4_1/a$	Non-ferroic	2
$P4/n$	$0, \frac{1}{2}, 0$	2	$P2/m; P2/b$	Ferroelastic	2
		2	$P4_2/m; P4_2/n$	Non-ferroic	2
	$\frac{1}{2}, \frac{1}{2}, 0$	2	$P2/b$	Ferroelastic	2
		2	$P4$	Ferroelectric	2
	$0, 0, \frac{1}{2}$	2	$P2_1/b$	Ferroelastic	2
		1	$P4/n; P4_2/n$	Non-ferroic	2
$P4_2/n$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	2	$B2/b$	Ferroelastic	2
		2	$I4$	Ferroelectric	2
	$\frac{1}{2}, \frac{1}{2}, 0$	2	$P2/b$	Ferroelastic	2
	$0, 0, \frac{1}{2}$	2	$P2_1/b$	Ferroelastic	2
$I4/m$	$\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$	2	$P4_1; P4_3$	Ferroelectric	2
		2	$P2_1/m; P2_1/b$	Ferroelastic	2
		1	$P4/m; P4_2/m; P4/n; P4_2/n$	Non-ferroic	2
	$\frac{1}{2}, \frac{1}{2}, 0$	2	$B2/m; B2/b$	Ferroelastic	2
		2	$P4/m; P4_2/m; P4/n; P4_2/n$	Non-ferroic	4
	$\frac{1}{2}, 0, 0$	4	$B2/m$	Ferroelastic	2
$I4_1/a$		4	$P1$	Ferroelastic	8
		4	$I4/m; I4_1/a$	Non-ferroic	8
	$\frac{3}{4}, \frac{1}{4}, -\frac{1}{4}$	2	$I4/m; I4_1/a$	Non-ferroic	4
	$\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$	2	$P2_1/b$	Ferroelastic	2
	$\frac{1}{2}, 0, 0$	4	$I4$	Higher-order ferroic	8
		4	$P1$	Ferroelastic	2
		4	$P1; B2/b$	Ferroelastic	4