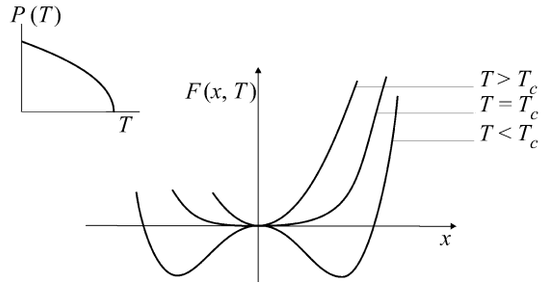

Fig. 3.1.5.1. Free energy $F(P, T)$ and order parameter $P(T)$ from the Landau–Devonshire theory [equation (3.1.5.1*a*)] for a continuous second-order ferroelectric phase transition [coefficient B positive in equation (3.1.5.1*a*)]. The insert shows the temperature dependence of the order parameter, *i.e.* the expectation value of the displacement $x(T)$.

continuous 'displacive' (as opposed to 'order–disorder') transitions, this order parameter is (or is proportional to) a normal mode of the lattice. One normal mode of the crystal must, in Cochran's theory, literally soften: the generalized force constant for this mode weakens as a function of temperature, and its frequency consequently decreases. This soft-mode theory provided an important step from the macroscopic description of Landau and Devonshire to a microscopic theory, and in particular, to vibrational (phonon) spectroscopy.

Cochran illustrated this theory using a 'shell' model in which the electrons surrounding an ion were approximated by a rigid sphere; shell–shell force constants were treated as well as shell–core and core–core terms, in the general case. The initial application was to PbTe and other rock-salt cubic structures that undergo ferroelectric structural distortions.

For this simple case, the key equations relate the optical phonon frequencies of long wavelength to two terms: a short-range force constant R_0' and a long-range Coulombic term. It is important that in general neither of these terms has a pathological temperature dependence; in particular, neither vanishes at the Curie temperature. Rather it is the subtle cancellation of the two terms at T_c that produces a 'soft' transverse optical phonon.

The longitudinal optical phonon frequency $\omega_{\rm LO}(T)$ is positive definite and remains finite at all temperatures:

$$\mu\omega_{\rm LO}^2 = R_0' + \frac{8\pi Z^2 e^2}{9\varepsilon V(T)}, \qquad (3.1.5.1b)$$

where μ is a reduced mass for the normal mode; Ze is an effective charge for the mode, related to the valence state of the ions involved; ε is the high-frequency dielectric constant and $V(T)$ is the unit-cell volume, which is a function of temperature due to thermal expansion.

By comparison, the transverse optical phonon frequency

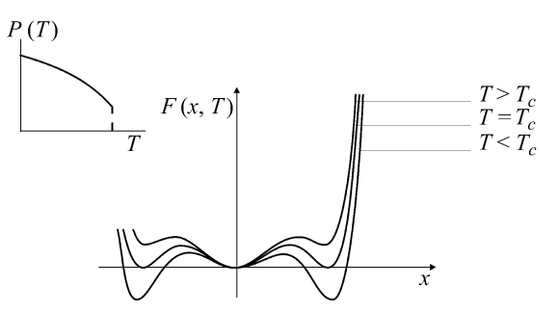

Fig. 3.1.5.2. Free energy $F(P, T)$ and order parameter $P(T)$ from the Landau–Devonshire theory [equation (3.1.5.1*a*)] for a discontinuous first-order ferroelectric phase transition [coefficient B negative in equation (3.1.5.1*a*)]. T_1 is the temperature (see Fig. 3.1.2.6) below which a secondary minimum appears in the free energy.

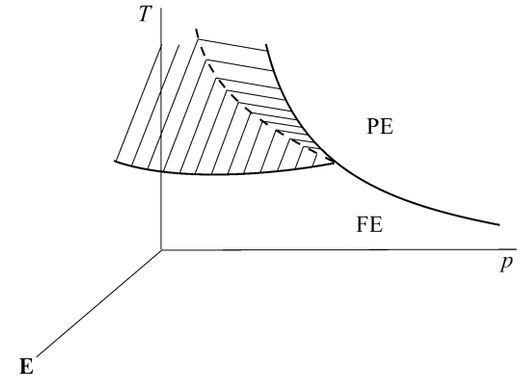

Fig. 3.1.5.3. Three-dimensional graph of phase boundaries as functions of temperature T, pressure p and applied electric field **E**, showing a tricritical point where three continuous phase boundaries intersect.

$$\mu\omega_{\rm TO}^2 = R_0' - \frac{4\pi Z^2 e^2}{3\varepsilon V(T)} \qquad (3.1.5.1c)$$

can vanish accidentally when $V(T)$ reaches a value that permits cancellation of the two terms. Note that this does not require any unusual temperature dependence of the short-range interaction term R_0'. This description appears to satisfy all well studied ferroelectrics except for the 'ultra-weak' ones epitomized by TSCC (tris-sarcosine calcium chloride), in which the Coulombic term in (3.1.5.1*b*) and (3.1.5.1*c*) is very small and the pathological dependence occurs in R_0'. This leads to a situation in which the longitudinal optical phonon is nearly as soft as is the transverse branch.

Subsequent to Cochran's shell-model developments, Cowley (1962, 1964, 1970) replaced this phenomenological modelling with a comprehensive many-body theory of phonon anharmonicity, in which the soft-mode temperature is dominated by Feynman diagrams emphasizing renormalization of phonon self-energies due to four-phonon interactions (two in and two out). This contrasts with the three-phonon interactions that dominate phonon linewidths under most conditions.

It is worth noting that the soft optical phonon branch is necessarily always observable in the low-symmetry phase *via* Raman spectroscopy in all 32 point-group symmetries. This was first proved by Worlock (1971), later developed in more detail by Pick (1969) and follows group-theoretically from the fact that the vibration may be regarded as a dynamic distortion of symmetry Γ_i which condenses at T_c to produce a static distortion of the same symmetry. Hence the vibration in the distorted phase has symmetry given by the product $\Gamma_i \times \Gamma_i$, which always contains the totally symmetric representation Γ_1 for any choice of Γ_i. If Γ_i is non-degenerate, its outer product with itself will contain only Γ_1 and there will be a single, totally symmetric soft mode; if Γ_i is degenerate, there will be two or three soft modes of different symmetries, at least one of which is totally symmetric.

Since the totally symmetric representation is Raman-active for all 32 point-group symmetries, this implies that the soft mode is always accessible to Raman spectroscopy at least in the distorted, low-symmetry phase of the crystal.

3.1.5.2.3. *Strontium titanate, $SrTiO_3$*

Among the perovskite oxides that are ferroelectric insulators, barium titanate has received by far the most attention from the scientific community since its independent characterization in several countries during World War II. The discovery of a ferroelectric that was robust, relatively inert (not water-soluble) and without hydrogen bonding was a scientific breakthrough, and its large values of dielectric constant and especially spontaneous polarization are highly attractive for devices. Although not ferroelectric in pure bulk form, strontium titanate has received

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