

# Chapter 1

## Ferroelectricity and Ferroelectric Phase Transition

Ultrathin crystalline films offer the possibility of exploring phase transitions in the crossover region between two and three dimensions. Second-order ferromagnetic phase transitions have been observed in monolayer magnetic films [1, 2] where the surface anisotropy energy stabilizes the two-dimensional ferromagnetic state at finite temperatures [3]. Similarly, a number of magnetic materials have magnetic surface layers that show a second-order ferromagnetic–paramagnetic phase transition with an increased Curie temperature [4]. Ferroelectricity is in many ways analogous to ferromagnetism, and bulk ferroelectricity and finite-size effects have been observed in nanocrystals as small as  $\sim 200$  Å in diameter [5, 6], and in thin films as thin as 100 Å [7]. First-order ferroelectric–paraelectric phase transitions in surface layers approximately 200 Å thick have been reported by Scott [8] and found to have enhanced transition temperatures. These results also can be interpreted as bulk ferroelectricity suppressed by the effects of surface energy and the depolarization field, and imply that the bulk ferroelectric state is associated with a minimum critical size [8–10]. Nevertheless, it is clear that the ferroelectric phase transition in the two-dimensional lattice is possible even in the simplest two-dimensional Ising model, as shown by Onsager in 1944 [11] and a little bit later by Landau [12].

Here we shall consider the main results of Landau-Ginzburg-Devonshire (LGD) mean field theory and the main principles of *ab initio* theory of ferroelectric phase transitions.

### 1.1 Landau-Ginzburg-Devonshire Mean Field Theory

Ferroelectric materials have fascinated scientists since their discovery in 1920 [13, 14]. In analogy with ferromagnets, the characteristic properties of ferroelectrics include spontaneous electric polarization, polarization reversal (switching), and disappearance of the polarization above a ferroelectric phase transition temperature  $T_c$ . Ferroelectric materials have been a fertile field for the

study of phase transitions, electron–phonon interactions, polaritons, and other optical and electrical phenomena in condensed matter.

From the time of the first reports of Valasek in the early 1920s [13, 14] many books and reviews have been devoted to the problem of ferroelectricity [15–19]. V. L. Ginzburg developed the first phenomenological theory ferroelectricity in the 1940s [20, 21] based on the Landau theory of second-order phase transitions [12, 22, 23] and a similar treatment was developed by Devonshire shortly thereafter [24–26].

Presuming that the order parameter in the Landau theory has the same transformation properties as the polarization vector  $P$ , we can in the uniaxial case express the Gibbs free energy density  $G$  in the Landau-Ginzburg polynomial expansion

$$G = F - EP = F_0 + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 - EP, \quad (1.1)$$

where  $F_0$  is the free energy density of the paraelectric phase (when  $E = 0$ ),  $E$  is the electric field, and the expansion coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  are in general temperature and pressure dependent. The equilibrium conditions correspond to the minimum of the free energy density, where

$$\frac{\partial F}{\partial P} = 0 \quad \text{and} \quad \frac{\partial^2 F}{\partial P^2} > 0. \quad (1.2)$$

The two main categories of ferroelectric materials are those that undergo a second-order transition, like triglycine sulfate (TGS), and those that undergo a first-order transition, like  $\text{BaTiO}_3$  and other perovskites.

In the Landau-Ginzburg theory of second-order ferro-electric phase transitions, the expansion coefficients have the values

$$\alpha = \frac{1}{\varepsilon_0 C}(T - T_0), \quad \beta < 0, \quad \gamma = 0, \quad (1.3)$$

where  $T_0 > 0$  is the Curie temperature,  $C > 0$  is the Curie–Weiss constant, and  $\varepsilon_0$  is the permittivity of free space. Applying the equilibrium conditions (1.2) and the coefficients (1.3) to the free energy density expansion (1.1), we obtain the value of the spontaneous polarization in the ferroelectric phase where

$$P_s = P(E = 0) = \pm \sqrt{\frac{\alpha}{\beta}} = \pm \sqrt{\frac{1}{\beta C^* \varepsilon_0}}(T - T_0)^{1/2}, \quad T < T_0. \quad (1.4)$$

The equilibrium temperature of transition from paraelectric to ferroelectric phase is  $T_c = T_0$ ; all properties are dependent on the difference between the crystal temperature  $T$  and the phase transition temperature  $T_c$ . The  $\pm$  signs indicate that the polarization can point in either direction along the symmetry axis (recall that this is the uniaxial case), and correspond to the two energetically equivalent states of the ferroelectric crystal at zero electric field. Equation (1.4) shows the typical

result that at the second-order ferroelectric phase transition there is no jump in the order parameter (the magnitude  $P_s$  in this case) and no latent heat of transition. However, there is a jump in the heat capacity.

The dielectric polarizability  $\chi$  in the paraelectric phase is built into the definition of  $\alpha$  and calculated from the free energy density expansion (1.1) and equilibrium conditions (1.2):

$$\frac{\partial^2 F}{\partial P^2} = \frac{1}{\chi} = \frac{T - T_0}{\varepsilon_0 C}.$$

The dielectric constant of the medium  $\varepsilon = \varepsilon_\infty + \chi/\varepsilon_0$  contains contributions from the background polarizability and the ferroelectric polarizability.

The general first-order phase transition is accompanied by a small but finite jump of the order parameter  $P$  and a transition enthalpy. Many ferroelectric materials exhibit a special kind of first-order phase transition with a change of symmetry from a group to subgroup, which is close to the situation in the second-order transition, and can be described by the free-energy density (1.1) with a negative  $P^4$  term (negative  $\beta$ ) and a nonzero  $P^6$  (positive  $\gamma$ ) term,

$$\alpha = \frac{1}{\varepsilon_0 C}(T - T_0), \quad \beta < 0, \quad \gamma > 0. \quad (1.5)$$

The phase transition temperature is

$$T_c = T_0 + \frac{3\varepsilon_0}{16}\beta^2 \frac{C}{\gamma},$$

and below this temperature the equilibrium spontaneous polarization is

$$P_s = P(E = 0) = \pm \sqrt{-\frac{\beta}{2\gamma} \left(1 + \sqrt{1 - t}\right)}, \quad T < T_0, \quad (1.6)$$

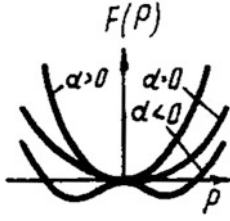
where the reduced temperature is

$$t = \frac{4\alpha\gamma}{\beta^2} = \frac{4\gamma(T - T_0)}{\varepsilon_0 C \beta^2}.$$

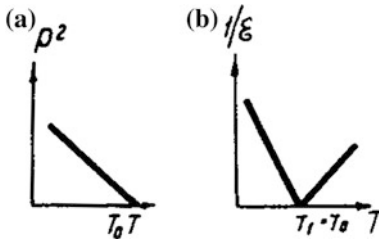
There is a jump in the magnitude of the spontaneous polarization from zero by  $\Delta P_s = \sqrt{-3\beta/4\gamma}$  at the phase transition temperature  $T_c$  (for  $E = 0$ ).

Figures 1.1 and 1.2 show the dependences free energy  $F$  on the parameters  $P$  and  $P^2$  and  $\varepsilon^{-1}$  on temperature  $T$  for the second and first order phase transition.

Another typical feature of the first-order phase transition is the temperature hysteresis and the metastable coexistence of both phases in the vicinity of the transition temperature  $T_c$ . The maximum temperature hysteresis in zero field  $\Delta T = \varepsilon_0 C \beta^2 / 4\gamma$  is a range bounded by  $T_0$ , the lower temperature limit for the metastable existence of the nonpolar state, and  $T_0 + \Delta T$ , the upper limit for the



**Fig. 1.1** Dependences  $F(P)$  near the temperature of the second-order phase transition



**Fig. 1.2** Dependences  $P_0^2(T)$ , and  $1/\epsilon(T)$  near the temperature of the second-order phase transition

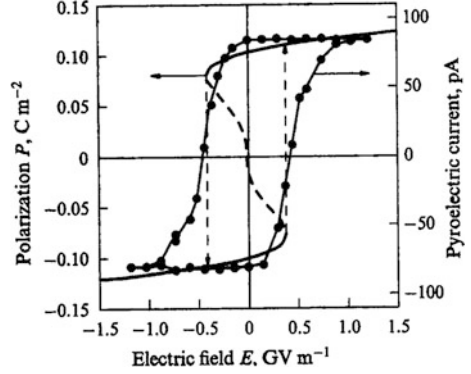
metastable existence of the polar state. The transition temperature  $T_c$  falls in between these two limits.

The electric field is calculated directly from the free energy density (1.1),

$$E = \frac{\partial G}{\partial P} = \alpha P + \beta P^3 + \gamma P^5. \quad (1.7)$$

This nonlinear dependence of the polarization  $P$  on the electric field  $E$  leads to a hysteresis loop, which is one of the key characteristics of ferroelectric materials. The hysteresis loop shown in Fig. 1.3 for the ferroelectric state ( $T < T_c$ ) illustrates the bistable nature of the polarization over a range of electric fields. The positive and negative values of the polarization correspond to the equivalent minima in the free energy. The intrinsic ferroelectric coercive field is the magnitude of the positive or negative electric field at which the polarization becomes single-valued and reverses direction, as shown in Fig. 1.3. The measured extrinsic coercive fields in real ferroelectric materials are orders of magnitude smaller than the intrinsic value calculated from the Landau-Ginzburg theory, because the theory does not take into account the extrinsic mechanism of local polarization reversal by nucleation followed by domain propagation and growth.

**Fig. 1.3** Measured hysteresis loop (points) and the theoretical relation  $P(E)$  [solid line, from Eq. (2.7)] for a ferroelectric polymer



The contribution of the polarization to the dielectric polarizability  $\chi$  in the paraelectric and ferroelectric phases is calculated from the electric field expression (1.7) as follows:

$$\frac{\varepsilon_0}{\chi} = \left[ \frac{\partial^2 F}{\partial P^2} \right] = \frac{T - T_0}{C}, \quad T > T_0,$$

$$\frac{\varepsilon_0}{\chi} = \left[ \frac{\partial^2 F}{\partial P^2} \right] = \frac{8(T - T_0)}{C} + \frac{9}{4} \frac{\beta^2}{\gamma}, \quad T < T_0 \quad (1.8)$$

It was mentioned above that the expansion coefficients of the free energy expansion (1.1) depend on temperature  $T$  and pressure  $p$ . Landau showed that, along the curve in the  $p, T$  diagram separating phases of different symmetry, there is a critical point  $p_{cr}, T_{cr}$  that marks the boundary between first and second-order phase transitions, that is, the coefficient  $\beta$  of the  $P^4$  term changes sign. The Landau-Ginzburg theory very well describes the anomalies near this co-called ‘critical Curie point’ or ‘tricritical point’ [27]. The first experimental observations of the tricritical point were reported in 1968 [28, 29]. In the first paper [28], it was shown that in SbSI crystals, which show a phase transition of the first order close to the second order one, the coexistence of ferroelectric and paraelectric phases vanishes as the tricritical point is approached from the region of the first-order transition.

It is important to underline, that strictly speaking LGD theory describes the phase transitions of the first order only in the vicinity of tricritical point. But from experimental point of view the concept of “vicinity” is very relative.

Spontaneous polarization may also occur in a crystal as a secondary effect as a consequence of more complicated changes in the crystal structure. In this case, the order parameter of the phase transition is not proportional to the polarization  $P$ , but to some other parameter, e.g., spontaneous deformation. In other words, the polarization is no longer the driving parameter of the transition, but it may arise or change as a consequence of structural changes. This type of phase transition is called an improper ferroelectric phase transition and the corresponding crystals are called improper ferroelectrics. The typical feature of the improper ferro-electric is

a change in the number of atoms in the unit cell volume at phase transition. Improper ferroelectric phase transitions can be modeled by the Landau-Ginzburg theory provided that the free energy expansion includes terms proportional to the true order parameter and cross terms between the order parameter and the polarization [19]. The inorganic oxide,  $\text{Gd}_2(\text{MoO}_4)_3$  [30] and ferroelectric liquid crystals [31] are examples of improper ferroelectrics.

All these thermodynamic results are complicated in real transitions by crystal nonuniformities, defects, grain boundaries, and domains. These complications have little effect on the phase transition but strongly influence polarization hysteresis (switching).

## 1.2 *Ab Initio* Theory of the Ferroelectric Phase Transition

$\text{BTiO}_3$  and other perovskites are ionic crystals. Here we do not consider the different models and microscopic theories for ionic, particularly perovskite, ferroelectrics (see i.e., [32]). For this purpose now are widely used *ab initio* calculations. The first *ab initio* calculations for ionic crystals were performed in the early 1930s. These calculations based on Thomas [33] and Fermi [34] the quantum-mechanical theory of many body systems. By this way Jensen and Lenz [35] calculated elastic constants and bulk moduli of several alkali-halide crystals.

The applications of the first principles calculations to the ferroelectric crystals were undertaken in last 20 years [36–39]. They used the density functional theory, developed by Kohn, Hohenberg and Sham [40]. In accordance with [40] the ground state of a crystal could be obtained from

$$\frac{dE_{el}\{\rho(r)\}}{d\rho(r)} = 0 \quad (1.9)$$

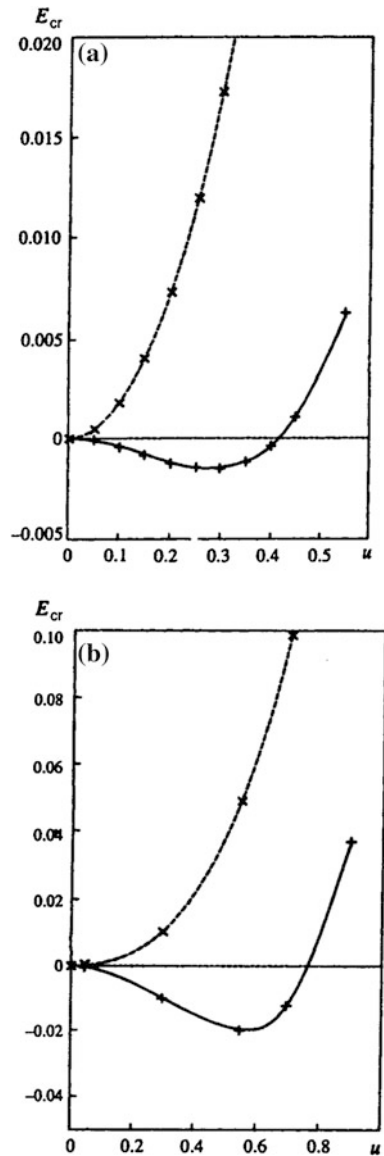
Here  $E_{el}$  is the total energy of the electrons in a crystal and  $\rho(r)$  in the particle (ion) density distribution. The energy  $E_{el}$  consists of four parts: Kinetic energy of the electrons, energy of interaction with an external field

$$V_{ext}(r) = \sum_n \frac{Z_n e^2}{|R_n - r|}$$

( $Z_n$  is the charge of the nucleus), energy of electron–electron interaction and energy of the exchange–correlation interaction of electrons.

$$\begin{aligned} E_{el}(\rho) = & \int \rho(r) E_k\{\rho(r)\} dr + \int V_{ext}(r) \rho(r) dr \\ & + e^2 \iint \frac{\rho(r) \rho(r')}{|r - r'|} dr dr' + \int \rho(r) E_{xc}\{\rho(r)^2\} dr \end{aligned} \quad (1.10)$$

**Fig. 1.4** Crystal energy  $E_a$  versus amplitude of the ferroelectric shift  $U$  in  $\text{BaTiO}_3$  (zero energy corresponds to the equilibrium value  $E_a^c$  in the *cubic* phase) in the “rigid ion” model (X) and in the self-consistent calculation (+); **a**—monopole, dipole, and quadrupole distortions of the charge density of the ions taken into account, **b**—only monopole and dipole distortions taken into account



In frame of the Kohn and Sham approximation, the density  $\rho(r)$  has form of the density of a certain system of noninteracting electrons placed in an external self-consistent field:

$$\rho(r) = \sum_i |\psi_i(r)|^2 \quad (1.11)$$

Functions  $\psi_i(r)$  are obtained from the Schrodinger equation:

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V_{eff}(r) \right] \psi_i = E_i \psi_i, \quad (1.12)$$

where effective potential  $V_{eff}$  has the form:

$$V_{eff} = V_{ext} + e^2 \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc}(r). \quad (1.13)$$

The exchange–correlation potential  $V_{xc}$  is given by (1.14):

$$V_{xc}(r) = \frac{dE_{xc}(\rho)}{d\rho}. \quad (1.14)$$

The exchange–correlation energy  $E_{xc}\{\rho(r)\}$  incorporates the contribution from potential and kinetic energy (see Eq. 1.10). The Kohn–Sham equations permit to obtain the phase transitions and changes in crystal properties, caused by the variations of the periodic wave functions. In [36] has been developed analogous to the Kohn–Sham method of the first principle calculations, based on a representation of the crystals electron density in the form of a sum of the densities of individual overlapping ions (rather than the density of a system of noninteracting electrons placed in a self-consistent periodic potential). On Fig. 1.4 the dependence of BaTiO<sub>3</sub> crystal energy  $E_{cr}$  as a function of Ti ion displacement is shown [36], demonstrating the first-order phase transition from the cubic to the tetragonal phase (see Fig. 1.2a).

The calculations done in [36] for the BaTiO<sub>3</sub> crystal have shown that in a distorted ferroelectric phase the values of the displacements of ions from their equilibrium positions in the cubic phase are in a good agreement with the experimental data only if one allows for both dipole and quadruple distortions in the electron density of the oxygen ions. Allowance for only dipole distortions overstates the value of ion displacements by a factor of almost two and overstates the decrease in the total energy in the ferroelectric phase by a factor of almost ten, as shown in Fig. 1.4.

Strictly speaking the results of *ab initio* theory in application to the ferroelectric phase transitions strongly depend on the value of the exchange–correlation potential  $V_{xc}$  (see 1.14), particularly on the effective charges and the interaction mechanism. Nevertheless the *ab initio* theory application for the critical size estimation a unique one (see Chap. 3).

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