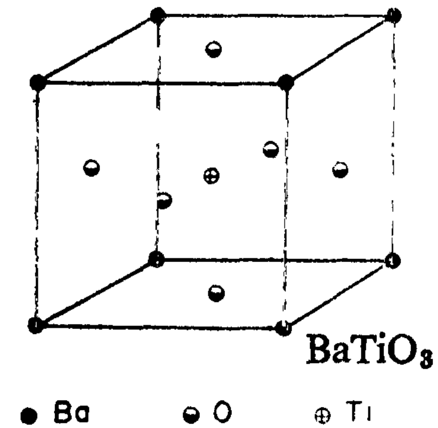
Landau theory of the phase transitions of the second kind

Some kind of symmetry is broken in the ordered state. There is an order parameter η, which is non-zero only in the state with broken symmetry. Examples: magnetization (in ferro- and antiferromagnetics), polarization in ferroelectrics, deviation of an atom from symmetric point (in structural transitions), wave function of Copper-pair condensate in superconductors, etc

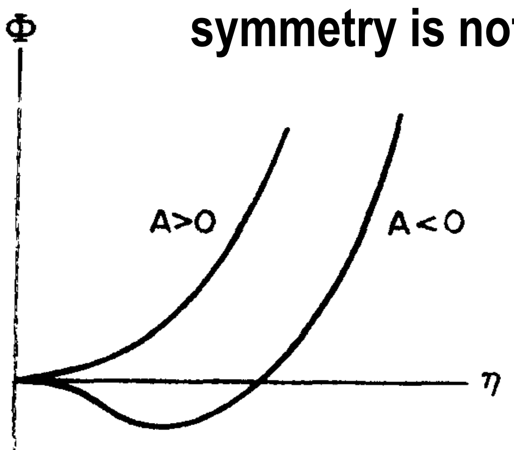


Thermodynamic potential (free energy) can be expanded in a series in order parameter η:

$$\Phi(P, T, \eta) = \Phi_0 + \alpha\eta + A\eta^2 + C\eta^3 + B\eta^4 + \ \ldots \qquad \alpha \equiv 0$$

where the coefficients α, A, B, C, ... are functions of P and T.

The order parameter η is not an independent variable, as P and T, but is determined from the minimization of the thermodynamic potential Φ. At T>Tc A>0 and η=0, i.e. symmetry is not broken, while T<Tc A<0 and η>0 and symmetry is broken.



At the transition point

$$A_c(P, T) = 0, \quad C_c(P, T) = 0, \quad B_c(P, T) > 0.$$

Knowledge of the free energy allows to find all thermodynamic quantities, including specific heat, which has a jump at Tc, the temperature dependence of the order parameter, etc.

Landau theory of the phase transitions of the second kind (2)

Usually the odd powers of the order parameter are absent in free energy (e.g., if η is a vector, as magnetization or electric polarization, and there is no external field):

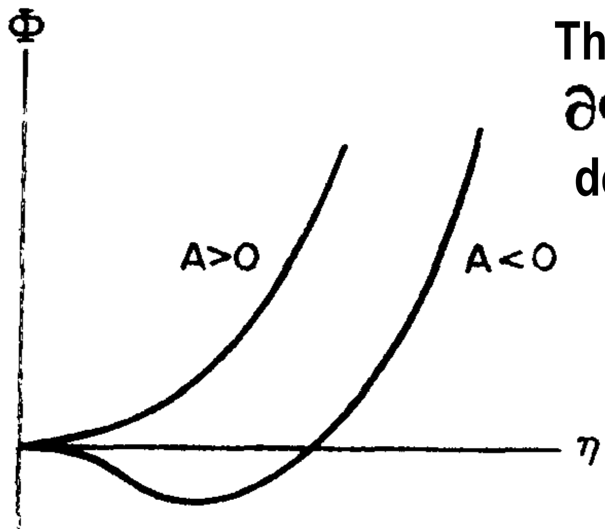
$$\Phi(P,T,\eta) = \Phi_0(P,T) + A(P,T)\eta^2 + B(P,T)\eta^4.$$

Here $B > 0$, while the coefficient $A > 0$ in the symmetrical phase and $A < 0$ in the unsymmetrical phase; the transition points are determined by the equation $A(P,T) = 0$.

Near the transition point the coefficient

$A(P,T) = a(P)(T - T_c)$, where $T_c = T_c(P)$ is the transition temperature.

$$\Phi(P,T) = \Phi_0(P,T) + a(P)(T - T_c)\eta^2 + B(P)\eta^4, \quad \text{with } B(P) > 0.$$



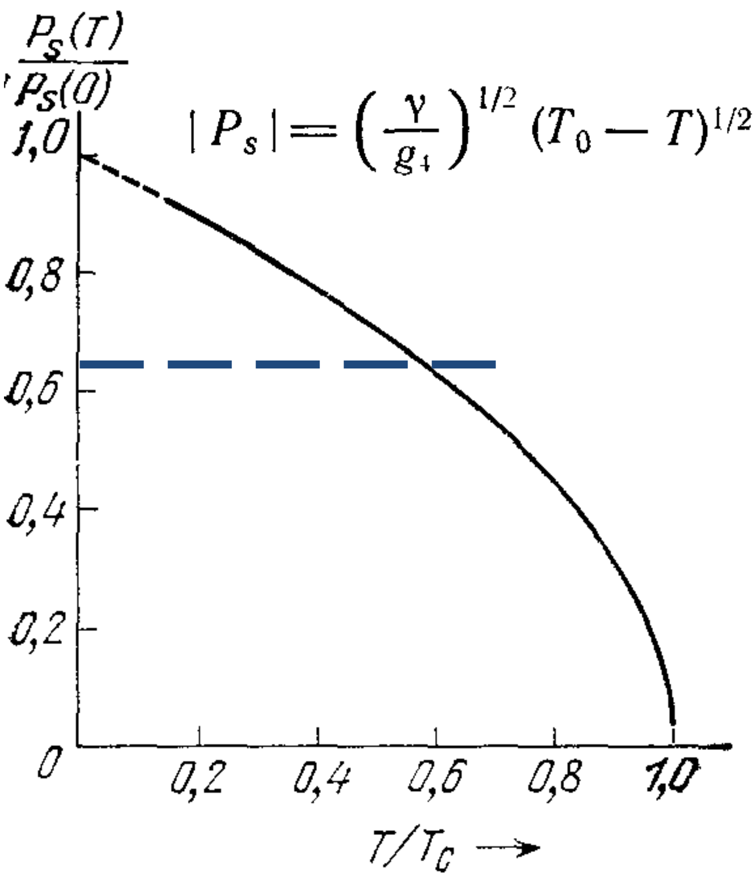
The minimum of the thermodynamic potential Φ is given by

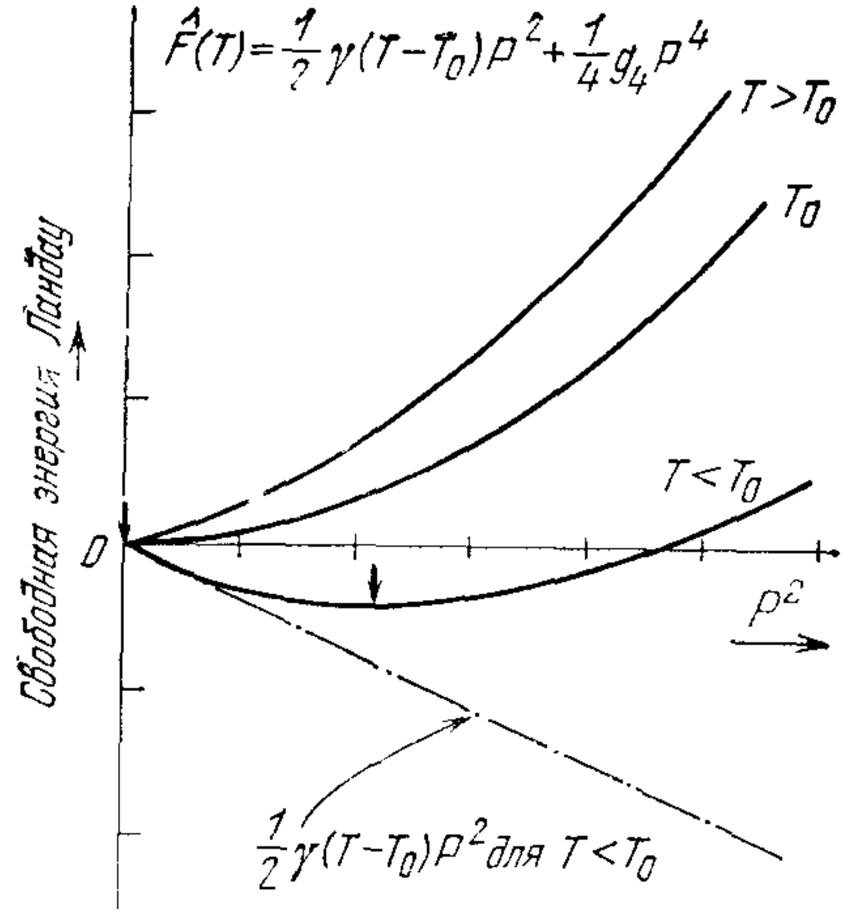
$\partial\Phi/\partial\eta = \eta(A + 2B\eta^2) = 0$, **which gives the temperature dependence of the order parameter**

$$\eta^2 = -A/2B = a(T_c - T)/2B$$

Examples: the temperature dependence of the order parameter in ferroelectrics

Theoretical predictions from the Landau theory of phase transitions

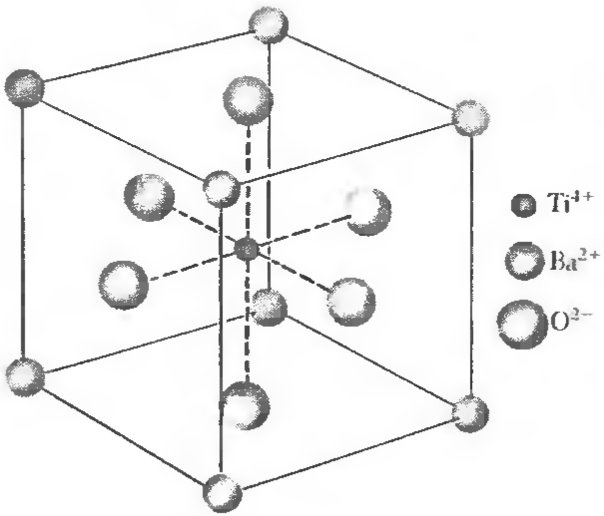


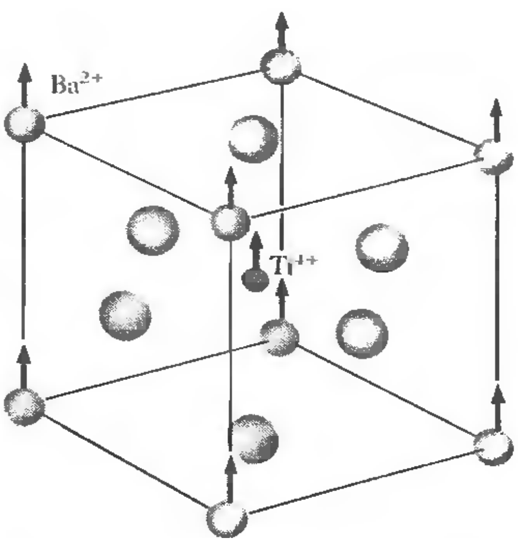


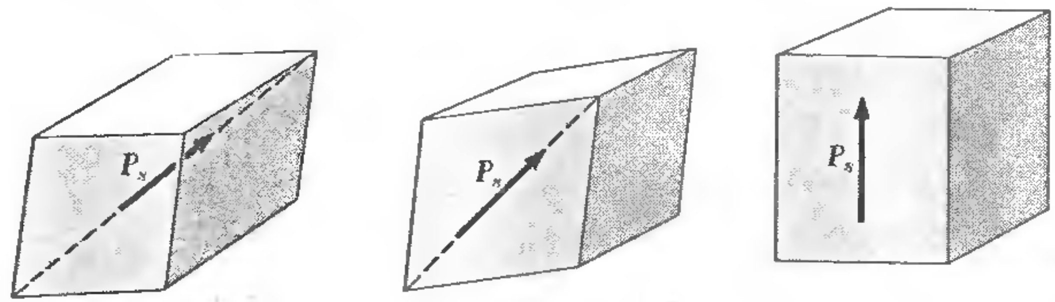
Examples: the temperature dependence of the order parameter in ferroelectric

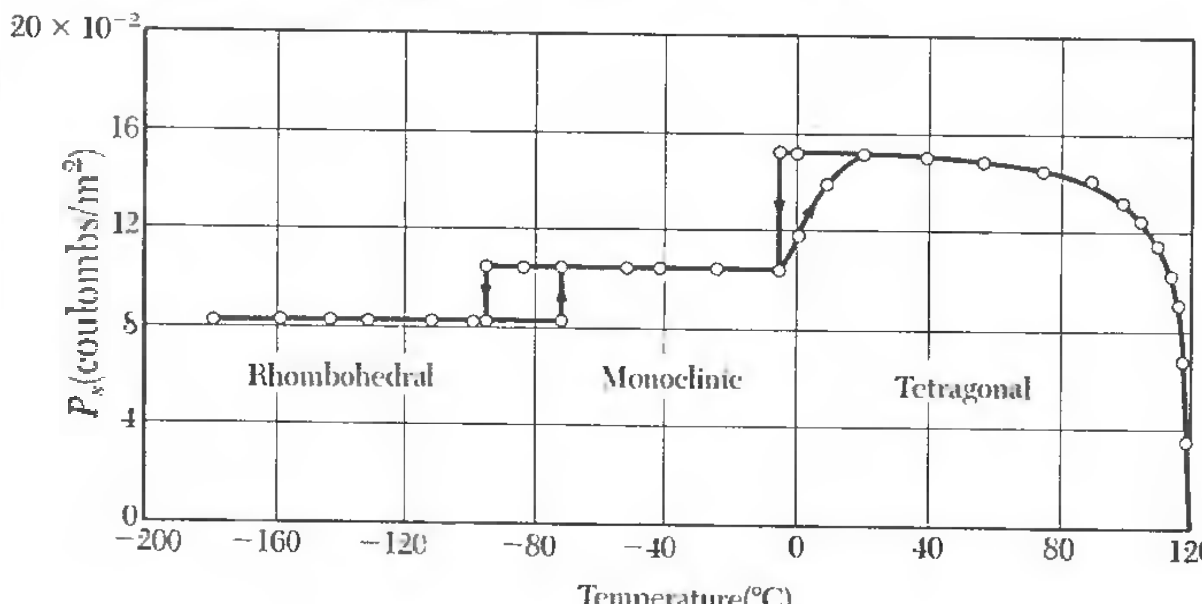
Theoretical predictions from the Landau theory of phase transitions

$$|P_s| = \left(\frac{\gamma}{g_4}\right)^{1/2} (T_0 - T)^{1/2}$$



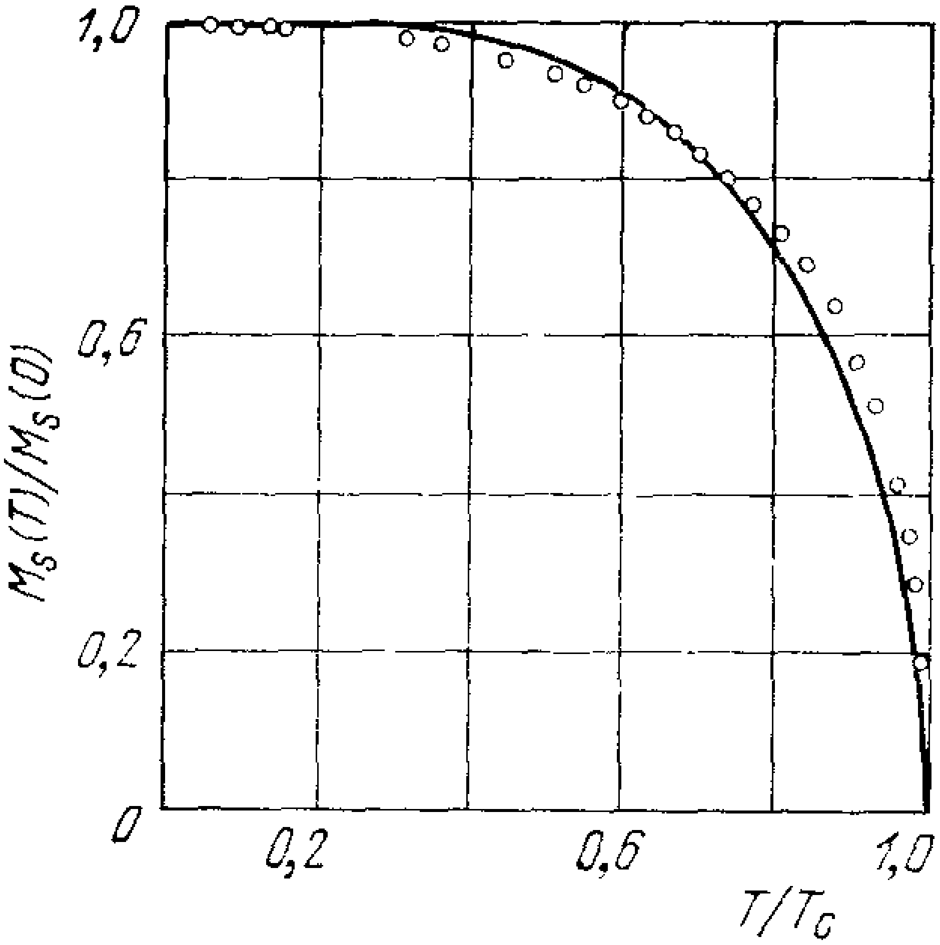






Spontaneous polarization projected on cube edge of barium titanate, as a function of temperature.

Examples: the temperature dependence of the order parameter in ferromagnetics



Saturation magnetization of nickel as a function of temperature, together with the theoretical curve for S = 1/2 based on the mean field theory.

Jump of specific heat at Tc

Thermodynamic potential is $\Phi(P,T,\eta) = \Phi_0(P,T) + A(P,T)\eta^2 + B(P,T)\eta^4.$

The entropy $S = -\partial\Phi/\partial T = S_0 - (\partial A/\partial T)\eta^2$, $\eta^2 = -A/2B = a(T_c - T)/2B$;

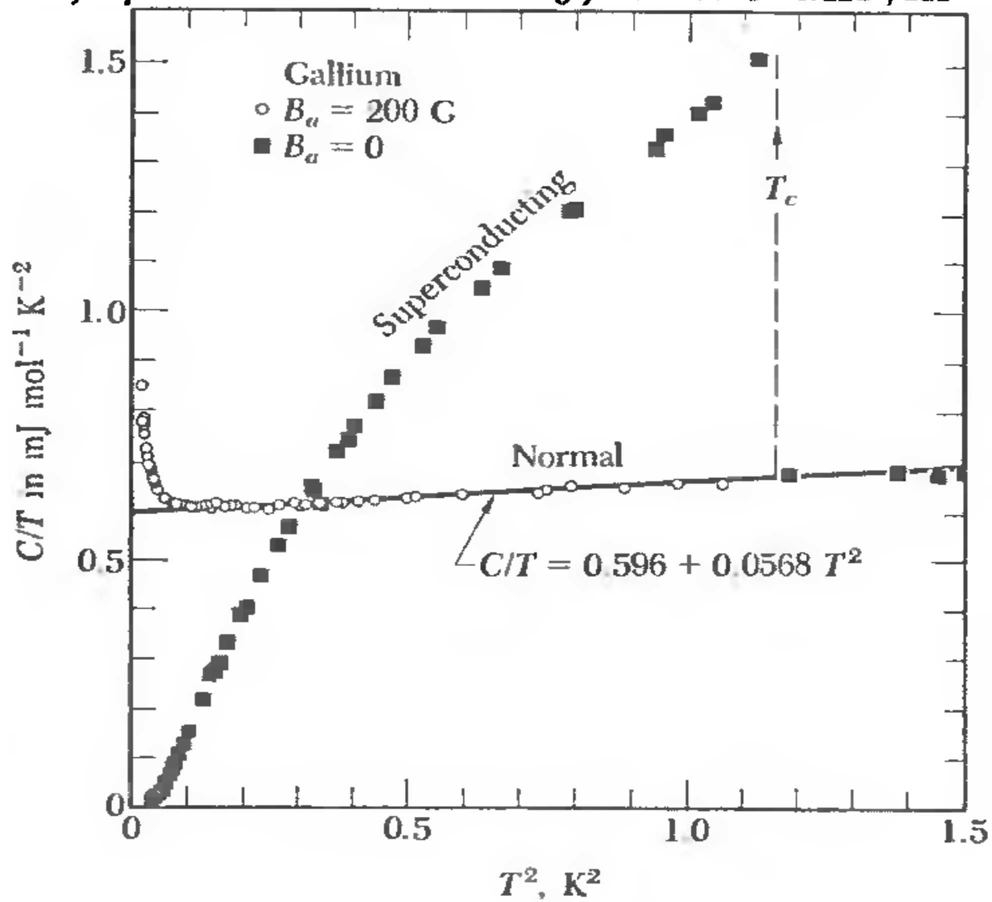
the term containing the temperature derivative of η is zero, because $\partial\Phi/\partial\eta = 0$. In the symmetrical phase, $\eta = 0$ and $S = S_0$; in the unsymmetrical phase,

$$S = S_0 + (a^2/2B)(T - T_c).$$

Specific heat in the unsymmetrical phase

$$C_p = T(\partial S/\partial T)_P = C_{p0} + a^2T_c/2B.$$

jump of specific heat at Tc

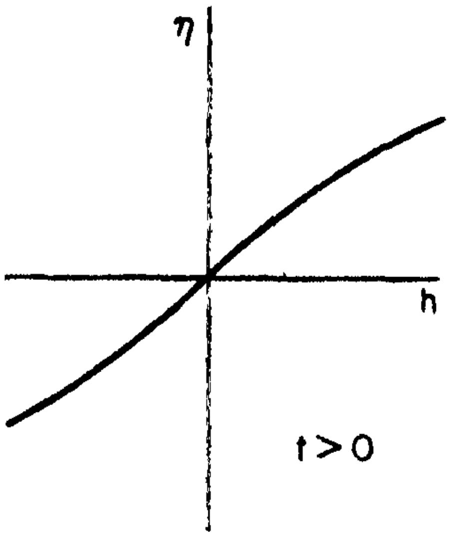


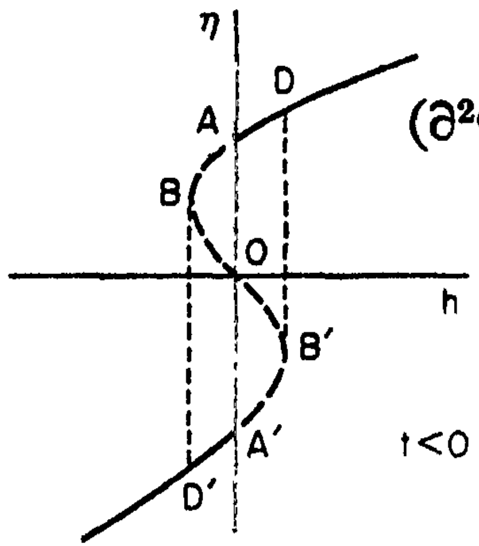
Landau theory of the phase transitions (of the second kind) in external field

The application of external field h is described by the appearance in the Hamiltonian of the body of a perturbing operator $\hat{H}_h = -\hat{\eta} h V,$ V is volume.

Thermodynamic potential becomes $\Phi(P, T, \eta) = \Phi_0(P, T) + at\eta^2 + B\eta^4 - \eta hV,$

The equilibrium condition $(\partial\Phi/\partial\eta)_{T,h} = 0$ gives $2at\eta + 4B\eta^3 = hV.$





instability region BB' when $(\partial^2\Phi/\partial\eta^2)_{T,h} < 0$ when $(\partial\eta/\partial h)_T < 0,$

The susceptibility is given by the derivative

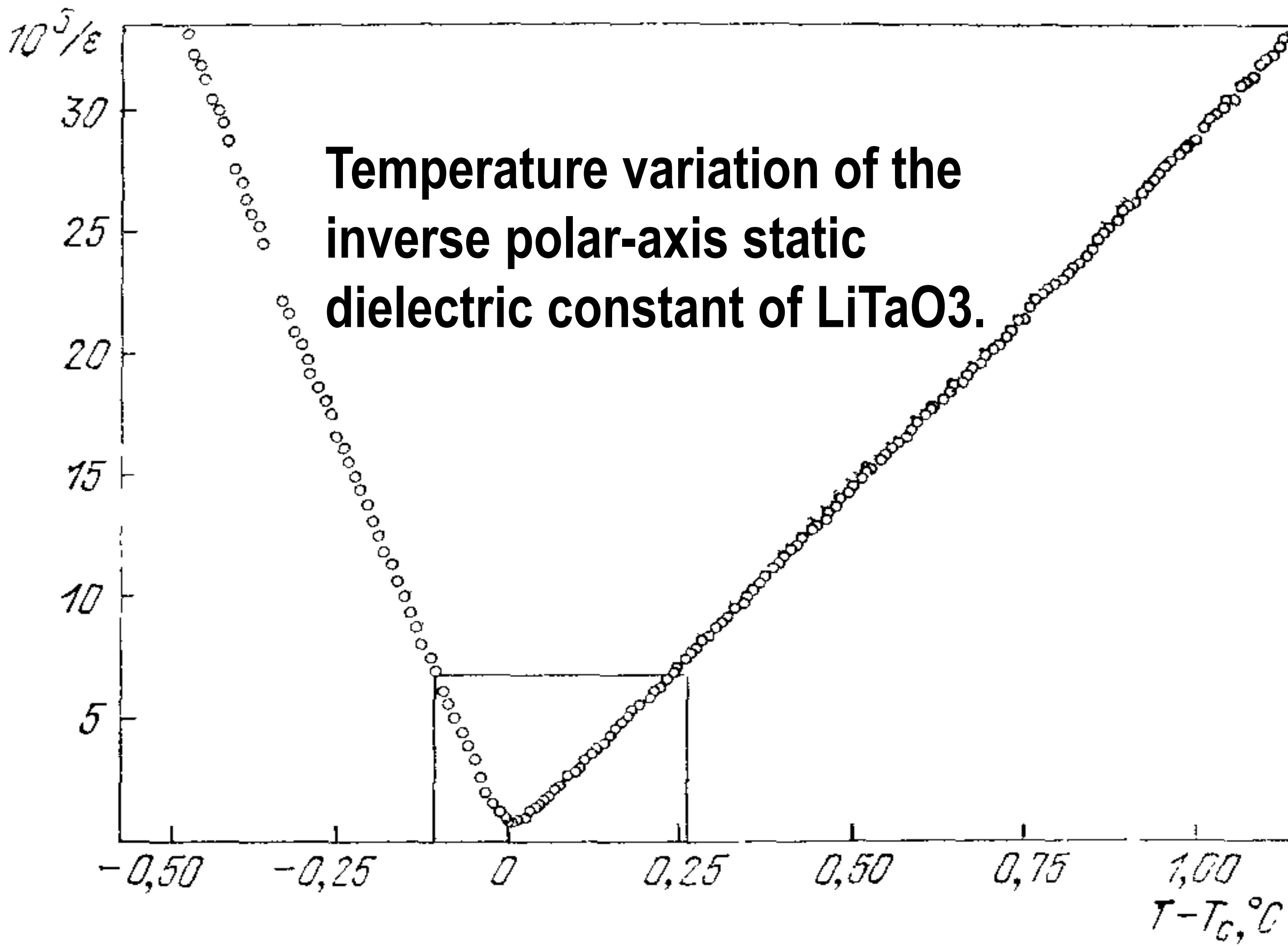
$$\chi = (\partial\eta/\partial h)_{T;\,h\to 0} = V/(2at + 12B\eta^2),$$

$$\eta^2 = -A/2B = a(T_c - T)/2B;$$

Result for susceptibility:

$$\chi = V/2at \quad \text{for} \quad t > 0, \qquad \chi = V/-4at \quad \text{for} \quad t < 0.$$

Example: temperature dependence of susceptibility in ferroelectric



Theoretical result for susceptibility: $\chi = V/2at$ for $t > 0$, $\chi = V/-4at$ for $t < 0$.

$$t = T - T_c(P).$$

Phase transitions of the first kind in terms of Landau theory

$$\Phi(P,T,\eta) = \Phi_0(P,T) + A(P,T)\eta^2 + B(P,T)\eta^4$$

If the coefficient B<0, the phase transition is of the first kind. Then one considers 6-order term in η. In this case the order parameter has a jump (not continuous increase from zero), and the specific heat diverges (has a sharp maximum instead of a jump).

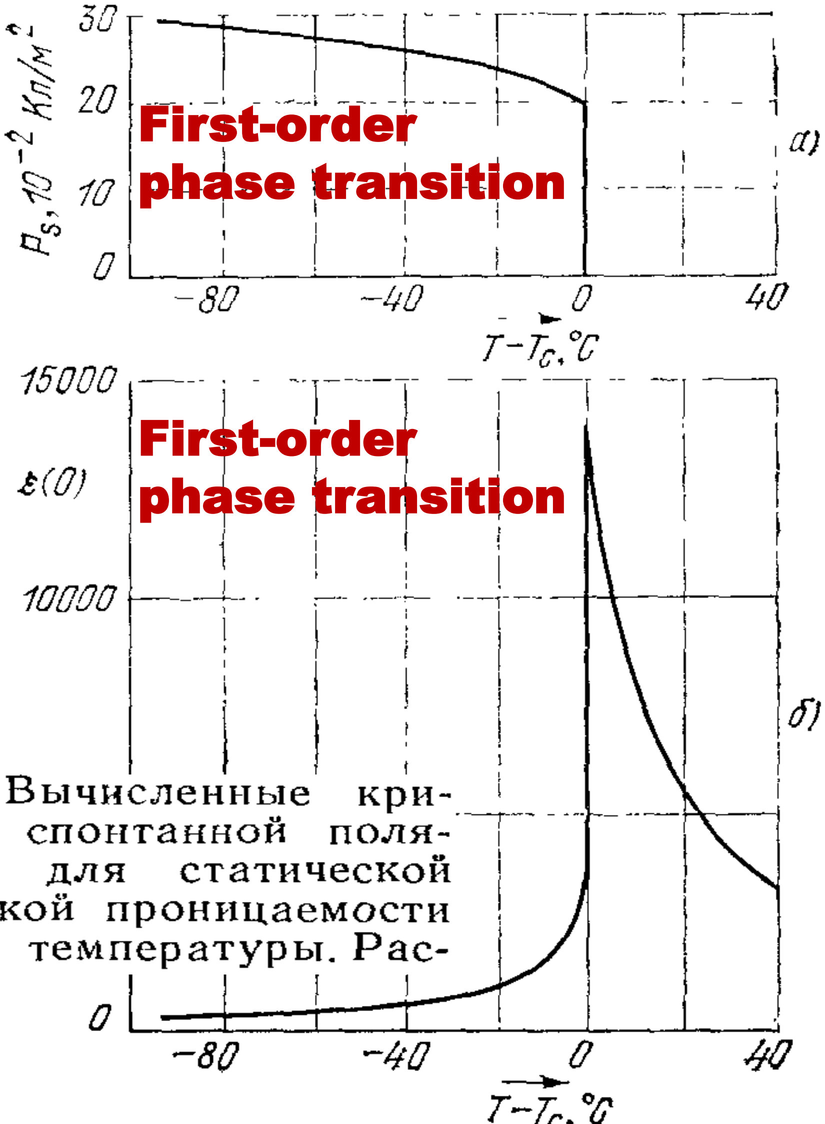


Рис. 14.10. Вычисленные кривые *а*) для спонтанной поляризации, *б*) для статической диэлектрической проницаемости как функции температуры. Рас-