Critical fluctuations and splitting of phase transition in a tetragonal ferroelectric

A. L. Korzhenevskiĭ and A. I. Sokolov

Leningrad Electrotechnical Institute

(Submitted 25 December 1977)
Pis'ma Zh. Eksp. Teor. Fiz. **27**, No. 5, 255–259 (5 March 1978)

It is shown that in an "easy-plane" tetragonal ferroelectric (ferromagnet) the interaction of strongly developed critical fluctuations can lead to a splitting of a continuous phase transition into two first-order transitions that are close to each other in temperature.

PACS numbers: 77.80.Bh

We wish to call attention in this article to an interesting effect that can be observed in anisotropic systems under conditions of strongly developed critical fluctuations. We have in mind a phase transition into a low-temperature phase which is not energywise most favored from the point of view of the Landau theory, as a result of which the phase transition should split into two transitions that are close to each other in temperature. The theory of this phenomenon is constructed below for the case of a tetragonal crystal of the "easy plane" type with dipole-dipole interaction. The choice of the model is governed by two factors. First, the critical thermodynamics of such systems has not yet been discussed in the literature, notwithstanding the many known ferroelectrics and ferromagnets that are tetragonal in the low-temperature phase. Second, the problem can be solved here analytically (without resorting to a computer), in contrast, say, to the case of a cubic crystal with dipole forces and an anistropic correlation function.

The effective Hamiltonian of the polarization-fluctuation field $\phi(\mathbf{q})$ in a tetragonal ferroelectric (ferromagnet), with account taken of only the essential invariants, is given by

$$H = \frac{1}{2}\sum_{\mathbf{q}}\Big\{\sum_{\alpha=1}^{3}(\kappa_0^2 + q^2 + f q_\alpha^2 + \Lambda_t^2\delta_{\alpha 3})\phi_\alpha(\mathbf{q})\phi_\alpha(-\mathbf{q}) + \sum_{\alpha,\beta=1}^{2}[(\Lambda^2 + h q^2)n_\alpha\phi_\alpha(\mathbf{q})$$

$$+(\Delta'^2 + h' q^2)n_3\phi_3(\mathbf{q})]n_\beta\phi_\beta(-\mathbf{q}) + (\Delta''^2 + h'' q^2)n_3^2\phi_3(\mathbf{q})\phi_3(-\mathbf{q})\Big\} + \frac{1}{4!}\sum_{\substack{\alpha\beta=1\\ \mathbf{q}+\mathbf{q}'+\mathbf{q}''+\mathbf{q}'''=0}}^{2}\Big\{[\gamma_2^{(0)}$$

$$(\gamma_1^{(0)} - \gamma_2^{(0)})\delta_{\alpha\phi}]\phi_\alpha(\mathbf{q})\phi_\alpha(\mathbf{q}')\phi_\beta(\mathbf{q}'')\phi_\beta(\mathbf{q}''')$$

$$[\gamma_3^{(0)}\phi_\alpha(\mathbf{q})\phi_\alpha(\mathbf{q}') + \frac{\gamma_4^{(0)}}{4}\phi_3(\mathbf{q})\phi_3(\mathbf{q}')]\phi_3(\mathbf{q}'')\phi_3(\mathbf{q}''')\Big\}. \quad (1)$$

ere $n_\alpha = q_\alpha/q$, the "mass" κ_0^2 depends linearly on the temperature, and the constants h, h', h'' are determined by the magnitude and form of the spatial dispersion of the short-range and dipole-dipole potentials. The tetragonal gap Δ_t and the dipole gaps Δ,Δ',Δ'' in the spectrum of the fluctuations characterize the anisotropy energy and the energy of the dipole-dipole interaction.

It is known that in ferroelectrics $\Delta,\Delta',\Delta'' \sim q_D \gg |\kappa_0|$, where q_D is the cutoff momentum. Let the crystal anisotropy be large enough, i.e., $\Delta_t \sim q_D$. Then the critical renormalizations of $\Delta,\Delta',\Delta'',\Delta_t$, which, just as the "mass" renormalization κ_0, are of the order of κ_0, can be neglected. The renormalizations of the dispersion parameters f,h,h',h'' are also negligibly small; they are known to be determined by the quantity $\partial\Sigma_{\alpha\beta}(0)/\partial q^2(\Sigma_{\alpha\beta}(\mathbf{q})$ is the mass operator), which is characterized by a numerical smallness of the same type as the smallness of the critical exponent η.[1] Taking all this into account, the Green's function $G_{\alpha\beta}(\mathbf{q})$ of our problem in the limit when $\kappa,q \ll \Delta,\Delta',\Delta'',\Delta_t$ can be represented in the form

$$G_{\alpha\beta}(\mathbf{q},\kappa) = \frac{[(1-n_3^2)\delta_{\alpha\beta} - n_\alpha n_\beta](1-\delta_{\alpha 3})(1-\delta_{\beta 3})}{(\kappa^2+q^2)(1-n_3^2) + 2fq^2n_1^2n_2^2}, \tag{2}$$

here κ is the reciprocal correlation radius (the renormalized "mass").

The critical thermodynamics of the system is determined by the form of the temperature dependences of the dressed coupling constants $\gamma_i = \Gamma_i(0,0,0,\kappa)$,[2,3] where $\Gamma_i(\mathbf{q},\mathbf{q}',\mathbf{q}'',\kappa)$ are the total vertices. The evolution of γ_i with changing temperature is described by the equations of the renormalization group (RG). An examination of the diagram expansions of the Gell-Mann–Low functions that enter in these equations reveals readily that under the assumption made above only two of the four RG equations are independent, those for γ_1 and γ_2, and the critical behavior of the two other coupling constants is uniquely determined by the temperature dependences of γ_1 and γ_2. We change from the vertices γ_i to the dimensionless invariant charges $g_i = \gamma_i/32\pi\kappa$. Then the RG equation for the charges g_1 and g_2 in three-dimensional space and in the lowest approximation in g_i, which is optimal in the present case,[4] will take the form

$$\frac{dg_1}{dt} = g_1 - 9I_1g_1^2 - 6I_2g_1g_2 - I_1g_2^2,$$

$$\frac{dg_2}{dt} = g_2 - 9I_2g_1^2 - 6I_1g_1g_2 - 9I_2g_2^2, \tag{3}$$

where

$$I_1 = \frac{1+f-\sqrt{1+f/2}}{f\sqrt{1+f/2}}, \quad I_2 = \frac{\sqrt{1+f/2}-1}{f\sqrt{1+f/2}}, \quad t = -\ln\kappa. \tag{4}$$

It is easily shown that all the singular points of the system (3) lie at the zeros of $g_2 = \xi g_1$, while ξ satisfies the equation

$$(\xi-\theta)(\xi^2+3) = 0, \qquad \theta = 3I_2/I_1. \tag{5}$$

Thus, the system (3) has one nontrivial singular point $g_1^* = 1/9(I_1+\theta I_2), g_2^* = \theta g_1^*$. This is a saddle point and lies on the "Heisenberg" line $g_2 = g_1$ at $f=0$. The picture of the

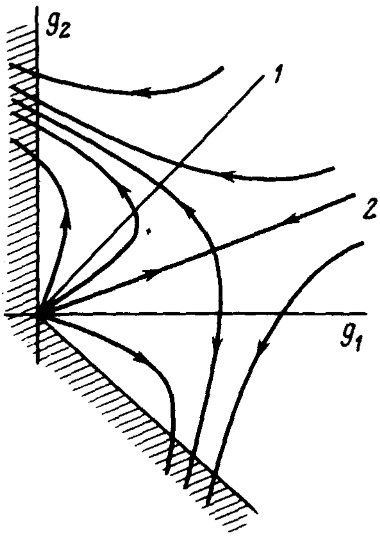

FIG. 1. Phase trajectories of the system of equations (3). The region of instability of the Hamiltonian (1) is shown shaded. The number 1 denotes the "Heisenberg" line $g_2=g_1$, and the number 2 denotes the separatrix $g_2=\theta g_1$, and the position of the separatrix corresponds to $f>0$.

phase trajectories of the system (3) is shown in Fig. 1. The parameter θ, which determines the slope of the separatrix $g_2=\theta g_1$, ranges from 3 to 0 when the anisotropy constant of the fluctuation spectrum f changes from -2 to ∞.[2)]

We see that at all values of the bare coupling constants the effective Hamiltonian becomes unstable in the critical region, and the phase transition in a tetragonal ferroelectric is of first order. Much more interesting, however, is the fact that the structure of the low-temperature phase can differ in this case from that predicted by the Landau theory. In fact, at $f\neq 0$ the inclination angle of the separatrix $g_2=\theta g_1$ is not equal to

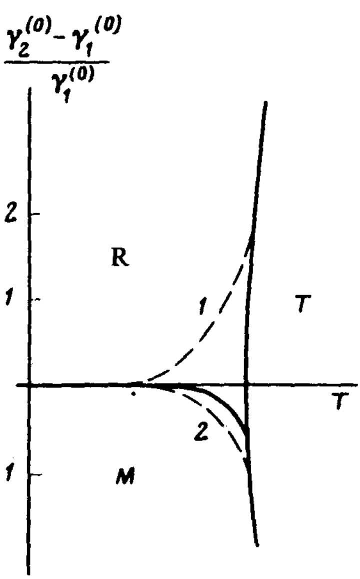

FIG. 2. Phase diagram of a tetragonal ferroelectric, shown as a plot of the anisotropy of the four-phonon anharmonic interaction vs temperature. The tetragonal (T), rhombic (R), and monoclinic (M) phases are separated from one another by first-order phase-transition lines. The shape of the "beak" corresponds to the slope of the separatrix on Fig. 1, and the dashed lines show the limiting positions of the "beak" at $f\to -2$ (1) and $f\to\infty$ (2).

45°, and there exist on the phase diagram trajectories that cross the "Heisenberg" line. This means that situations are possible in which the crystal, having a binding-constant bare anisotropy of the "rhombic" type, will go over after the phase transition into a monoclinic phase and vice versa. At the same time it is clear that far from the critical region the thermodynamically stable phase is the one predicted by the Landau theory. It follows therefore that with decreasing temperature a second phase transition should occur in the crystal—from one low-temperature phase (non-Landau) to another. This transition obviously should be of first order. An idea of the topology of the phase diagram of a tetragonal ferroelectric in the described case is provided by Fig. 2. The critical fluctuations and the anisotropy of the dispersion of the correlation function lead to the appearance on this diagram of a characteristic "beak" formed by the first-order phase-transition lines.

The effect of splitting of the phase transition is not restricted to the model considered here. This phenomenon should be observed in a large number of other cases, when a first-order phase transition takes place under conditions of strongly developed critical fluctuations and the correlation of these fluctuations is anisotropic at finite q. For example, in those ferromagnets and antiferromagnets where the interaction of the fluctuations of the order parameter leads to a change in the type of the phase transition,[5,7] the anisotropy of the exchange interaction can cause splitting of this transition into two. In this case the separatrices in the space of the invariant charges will not coincide, as above, with the high-symmetry lines (of the "Heisenberg" type), and "beaks" will appear on the phase diagrams.

We thank S. L. Ginzburg and S. V. Maleev for a discussion of the results.

[1)]Actually the renormalizations of f, h: h',h'' become noticeable only in a very narrow and practically unattainable vicinity of T_c.[1]

[2)]As seen from (2), the phase transition will go into a homogeneous (ferroelectric) phase only at values of f in the interval $(-2,\infty)$.

1T. Natterman, J. Phys. C9, 3337 (1976).
2A.Z. Patashinskiĭ and V.L. Pokrovskii, Usp. Fiz. Nauk **121**, 55 (1977) [Sov. Phys. Usp **20**, 31 (1977)].
3E. Brezin, J.C. LeGuillou, J. Zinn-Justin, in: Phase Transitions and Critical Phenomena, Vol. 6, Academic, 1976.
4A.I. Sokolov, Fiz. Tverd. Tela (Leningrad) **19**, 747 (1977) [Sov. Phys. Solid State **19**, 433 (1977)].
5D. Mukamel, S. Krinsky, J. Phys. **C8**, L496 (1975); Phys. Rev. **B13**, 5078 (1976).
6S.A. Brazovskiĭ, I.E. Dzyaloshinskiĭ, and B.G. Kukharenko, Zh. Eksp. Teor. Fiz. **70**, 2257 (1976) [Sov. Phys. JETP **43**, 1178 (1976)].
7I.E. Dzyaloshinskiĭ, ibid. **72**, 1930 (1977) [**45**, 1014 (1977)].