Scaling invariance and first-order phase transitions in cubic ferroelectrics

A. I. Sokolov

Leningrad Electrotechnical Institute
(Submitted June 4, 1975)
ZhETF Pis. Red. 22, No. 4, 199–203 (August 20, 1975)

The phase transition in a three-dimensional model with dipole-dipole interactions is considered in the quadratic approximation for the Gell-Mann–Low functions. It is shown that the phase transition is of first order in the presence of an arbitrarily weak cubic anisotropy.

PACS numbers: 77.80.B

It was noted long ago that phase transitions in ferroelectric crystals are usually of first order and are close to second order. The best known example of this type is the phase transition from the cubic phase into the tetragonal phase in barium titanate. It is customarily assumed that this phenomenon is due to the influence of electrostriction on the critical thermodynamics of the crystal.[1,2] The electrostriction mechanism of the transformation of the continuous phase transition into a first-order transition is, however, not the only one. As will be shown below, in the presence of dipole-dipole interaction (which always exists in ferroelectrics), the cause of the change in the order of the transition may be the cubic anisotropy of the crystal, which can furthermore be arbitrarily weak.

The Hamiltonian of a cubic ferroelectric in the critical region is taken in the form

$$H = \frac{1}{2}\sum_{\alpha\beta\mathbf{q}} [(r_0 + q^2)\,\delta_{\alpha\beta} + \Delta^2 n_\alpha n_\beta]\,\phi_\alpha(\mathbf{q})\,\phi_\beta(-\mathbf{q}) + \frac{1}{4!}\sum_{\substack{\alpha\beta \\ \mathbf{q}+\mathbf{q}'+\mathbf{q}''+\mathbf{q}'''=0}} [2\gamma_2 + (\gamma_1 - 2\gamma_2)\,\delta_{\alpha\beta}]\,\phi_\alpha(\mathbf{q})\,\phi_\alpha(\mathbf{q}')\,\phi_\beta(\mathbf{q}'')\,\phi_\beta(\mathbf{q}'''), \qquad n_\alpha = q_\alpha / q. \tag{1}$$

The vector field ϕ_α corresponds to the critical branches of the spectrum of the system, while the bare "mass" r_0 depends linearly on the temperature. The energy of the dipole-dipole interaction[2,3] is determined by the parameter Δ, which is of the order of the cutoff momentum q_D in ferroelectrics, where this interaction is strong.

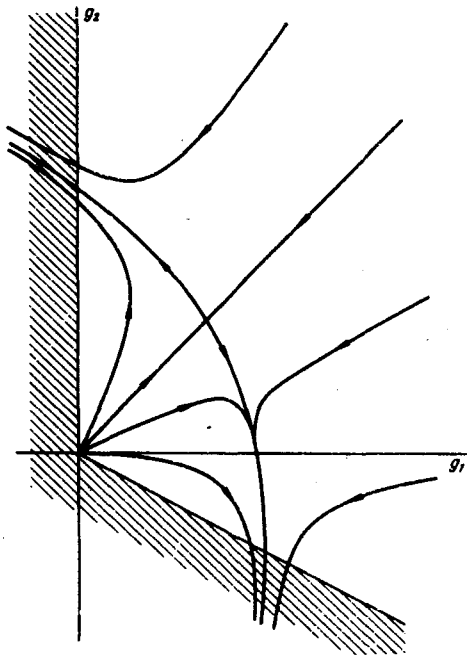
The question of the order of the phase transition can be resolved by determining the character of the evolution of the renormalized coupling constants Γ_1 and Γ_2 as functions of the temperature as $T \to T_c$.[4–6] This evolution is described by the equations of the renormalization group. It is known, however, that the Gell-Mann–Low functions which enter in these equations cannot be calculated exactly, and can be approximated in the region of interest to us by segments of power-law series only for $(4-\epsilon)$-dimensional models, where $\epsilon \ll 1$.[7] At the same time, if dipole-dipole interaction is present in the system, the dimensionality of the field ϕ_α must be assumed to be equal to the dimensionality of $\mathbf{q}$-space.[3] Consequently, working within the framework of the ϵ expansion, we are forced to consider only a "partially anisotropic" crystal, in which only three components of the field ϕ_α are "enclosed by anisotropy" in the Hamiltonian (1), and the remaining $(1-\epsilon)$ components remain "isotropic" (see, e.g.,[8]). The reliability of the results obtained by analytic continuation in ϵ then turns out to be quite doubtful, inasmuch as the symmetry of the Hamiltonian changes at the point $\epsilon = 1$, where the anisotropy becomes "complete." On the other hand, it was recently observed[9] that even a quadratic-in-Γ approximation of the Gell-Mann–Low function yields directly, in spite of the lack of general-theoretical premises, perfectly satisfactory results for the Heisenberg three-dimensional model. Therefore, bearing in mind the shortcomings of the ϵ expansion, we shall consider directly the three-dimensional case, hoping to obtain at least a qualitatively correct picture.

In our case, the correlation function $G_{\alpha\beta}(\mathbf{q})$ and the mass operator $\Sigma_{\alpha\beta}(\mathbf{q})$ are obviously not diagonal. Recalling, however, that $G_{\alpha\beta}(\mathbf{q})$ coincides with the susceptibility, we can easily obtain for it, as small values of q, the representation

$$G_{\alpha\beta}(\mathbf{q}) = \frac{\delta_{\alpha\beta} - n_\alpha n_\beta}{r_0 + q^2 - \Sigma(q)} + \frac{n_\alpha n_\beta}{r_0 + \Delta^2 + q^2 - \Sigma(q)}, \qquad \Sigma(q) \equiv \Sigma_{\alpha\alpha}(q). \tag{2}$$

Since $\Delta \sim q_D$, the longitudinal component of $G_{\alpha\beta}(\mathbf{q})$ can be neglected. Further operations on the derivation of the equations of the renormalization group are quite standard.[7,9] Making two subtractions and confining ourselves in (2) to the pole term, we obtain, neglecting η,

$$G_{\alpha\beta}(\mathbf{q}) \simeq \frac{\delta_{\alpha\beta} - n_\alpha n_\beta}{r + q^2}. \tag{3}$$



Phase trajectories of the system (4). The region of instability of the Hamiltonian (1) is shown shaded.

Expanding further the derivatives $d\Gamma_1/dr$ and $d\Gamma_2/dr$ in a renormalized diagram series with propagators (3) and separating the scaling asymptotic forms $\Gamma_1 = 120\pi\sqrt{r}g_1$ and $\Gamma_2 = 120\pi\sqrt{r}g_2$, we arrive at the Gell-Mann–Low equations for $g_1(r)$ and $g_2(r)$. Accurate to second order, these equations take the form

$$\frac{dg_1}{dt} = -\frac{g_1}{2} - 24g_1^2 - 4g_1g_2 - 6g_2^2, \qquad \frac{dg_2}{dt} = \frac{g_2}{2} - 3g_1^2 - 18g_1g_2 - 13g_2^2, \quad t = -\ln r. \tag{4}$$

The investigation of the system (4) is elementary. It has two singular points: $g_1 = g_2 = \frac{1}{68}$ and $g_1 = g_2 = 0$. The first of them is a saddle point and the second is an unstable node. The phase trajectories of the system are shown in the figure. It is clearly seen that all the trajectories with the exception of the "Heisenberg" trajectory ($g_1 = g_2$) go off beyond one of the boundaries of the stability region given by the equation $g_1 = 0$ and $g_1 = -2g_2$. Thus, in the presence of even very weak anisotropy, the phase transition is of first order. The latter is typical precisely of systems with dipole-dipole interaction. Indeed, it can be shown that a cubic crystal with a short-range potential and three-dimensional order parameter experiences a first-order phase transition only at sufficiently strong bare anisotropy, namely, when $\gamma_2 < 0$ or $\gamma_2 > 3\gamma_1/2$.

We note in conclusion several singularities of the phase transition in the model (1), which are typical also of the transition in barium titanate. First, in our case the character of the phase transition is determined by the interaction of the critical fluctuations, i.e., the transition takes place, just as in $BaTiO_3$,[2] in the region of strong correlation effects. Second, as seen from the figure, the effective anisotropy of the model increases as T_c is approached. The growth of the anisotropy of the critical fluctuations in the region of the phase transition in barium titanate was also noted many times by experimentors.[10] It is not excluded therefore that the fact that the phase transitions in $BaTiO_3$ and in other perovskites are of first order is due, at least in part, to the effect of the mechanism considered above.

I am grateful to S. L. Ginzburg and S. V. Maleev for a discussion of the results of the work.

[1]A. I. Larkin, and S. A. Pikin, Zh. Eksp. Teor. Fiz. **56**, 1664 (1969) [Sov. Phys.-JETP **29**, 891 (1969)].
[2]V. G. Vaks, Vvedenie v mikroskopicheskuyu teoriyu segnetoélektrikov (*Introduction to the Microscopic Theory of Ferroelectrics*), Nauka, 1973.
[3]A. Aharony and M. E. Fisher, Phys. Rev. **B8**, 3323 (1973).
[4]K. GA Wilson and M. E. Fisher, Phys. Rev. Lett. **28**, 240 (1972).
[5]I. F. Lyuksyutov and V. L. Pokrovskiĭ, ZhETF Pis. Red. **21**, 22 (1975) [JETP Lett. **21**, 9 (1975)].
[6]S. A. Brazovskiĭ and I. E. Dzyaloshinskiĭ, ZhETF Pis. Red. **21**, 360 (1975) [JETP Lett. **21**, 164 (1975)].
[7]T. Tsuneta and E. Abrahams, Phys. Rev. Lett. **30**, 217 (1973).
[8]A. Aharony, Phys. Rev. **B8**, 3358 (1973).
[9]S. L. Ginzburg, Zh. Eksp. Teor. Fiz. **68**, 273 (1975) [Sov. Phys.-JETP **41**, No. 1 (1975)].
[10]Y. Yamada, G. Shirane, and A. Linz, Phys. Rev. **177**, 848 (1969); J. Harada, J. Axe, and G. Shirane, Phys. Rev. **B4**, 155 (1971).