

PHASE TRANSITION IN UNIAXIAL FERROELECTRICS

A. I. LARKIN and D. E. KHMEL'NITSKIĬ

Institute of Theoretical Physics, U.S.S.R. Academy of Sciences

Submitted January 16, 1969

Zh. Eksp. Teor. Fiz. 56, 2087-2098 (June, 1969)

The form of the singularity of thermodynamic quantities at the phase transition point in a uniaxial ferroelectric substance is determined. The results differ from the predictions of the phenomenological theory by logarithmic factors. Similar results have been obtained for four-dimensional models discussed in Appendix 2.

1. INTRODUCTION

THE phase transition in uniaxial ferroelectrics has essential singularities because in these crystals there is a long-range dipole-dipole interaction. Such an interaction weakens the fluctuations of the dipole moment. In the region of applicability of the phenomenological theory the correlation function is of the form<sup>[1]</sup>

$$\langle P_z(\mathbf{k})P_z(-\mathbf{k}) \rangle \sim (|T - T_c| + \alpha k^2 + \beta k_z^2 / k^2)^{-1} \quad (1)$$

and increases as one approaches the transition point only for wave vectors lying in the basal plane. The corrections to the thermodynamic functions, connected with these fluctuations, are proportional to the integral of the square of the correlation function. Because of the presence of an angular dependence, these integrals are proportional not to a power but to  $\ln |T - T_c|$ .<sup>[2,3]</sup> The following approximations are proportional to powers of logarithms recalling the situation in quantum field theory where methods have been developed<sup>[4,5]</sup> which make it possible to obtain logarithmically exact results. These methods are applied to an evaluation of thermodynamic functions in the vicinity of the phase transition. As a result it turns out that the effective interaction decreases as one approaches the transition point in analogy with the result of the "zero charge" in quantum field theory.<sup>[4]</sup> The temperature dependences of the specific heat, susceptibility, and the spontaneous moment have been obtained. The results obtained differ from the predictions of the phenomenological theory by logarithmic factors. In the case in which there exists a small parameter, on going away from the Curie point the obtained results go over to the formulas of the phenomenological theory.

The problem of the phase transition in a ferroelectric is formally analogous to the four-dimensional problem where the role of the fourth component of the momentum is played by the quantity  $k_z/k$ . Four-dimensional models turn out to be convenient for clarifying what the singularities in the thermodynamics depend on. In Appendix 2 we consider models with various symmetries of the Hamiltonian.

2. DISPLACEMENT-TYPE TRANSITION. THE HAMILTONIAN

In displacement-type ferroelectrics the transition is accomplished as a result of a peculiar Bose-Einstein condensation in a gas of weakly interacting optical

phonons.<sup>[6,7]</sup> A uniaxial transition corresponds to the condensation of phonons with the polarization along the ferroelectric axis. The most important contribution to the various parts of the thermodynamic quantities is due to low-frequency phonons whose occupation numbers are large. Such phonons can be considered classically, even if the transition temperature  $T_c$  is of the order of the Debye temperature. Therefore, the Hamiltonian which describes these phonons is of the form

$$H = \frac{1}{2} \sum_i \alpha \xi_i^2 + \frac{1}{2} \sum_{ij} V_{ij} (\xi_i - \xi_j)^2 + \frac{e_{\text{eff}}^2}{2} \sum_{i \neq j} \frac{\partial^2}{\partial z_i^2} \frac{\xi_i \xi_j}{|r_i - r_j|} + \frac{b}{4!} \sum_i \xi_i^4, \quad (2)$$

where  $\xi_j$  is the displacement of the ions in the  $i$ -th unit cell, and  $V_{ij}$  is the short-range part of their interaction with one another. The last term describes the anharmonic interaction between the phonons. For displacement-type transitions it is essential that  $\xi$  be small compared with the interatomic distances and one can therefore restrict oneself to a simpler form of anharmonicity.

In going over to the momentum representation we take into account the fact that wave vectors  $\mathbf{k}$  much smaller than the reciprocal lattice vectors are important in the problem. The contribution of phonons with such  $\mathbf{k}$  to the Hamiltonian is

$$H = \frac{1}{2} \sum_{\mathbf{k}} \left( \mu + s k^2 + \lambda \frac{k_z^2}{k^2} \right) \xi_{\mathbf{k}} \xi_{-\mathbf{k}} + \frac{b}{4!N} \sum_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4 = 0} \xi_{\mathbf{k}_1} \xi_{\mathbf{k}_2} \xi_{\mathbf{k}_3} \xi_{\mathbf{k}_4}$$

Here  $\mu = a - \lambda/3$ ,  $\lambda = 4\pi e_{\text{eff}}^2 / v_{\text{un}}$ , and  $v_{\text{un}}$  is the volume of a unit cell.

In a ferroelectric  $\mu$  is anomalously small and negative; the anharmonic term is therefore important.

All physical quantities will be calculated by expanding in  $b$  and summing the important terms of the series. Let us, for example, consider the Green's function<sup>[8]</sup>

$$G(\mathbf{k}) = \frac{1}{T} \langle \xi_{\mathbf{k}} \xi_{-\mathbf{k}} \rangle. \quad (4)$$

In the harmonic approximation

$$G_0(\mathbf{k}) = (\mu + s k^2 + \lambda x^2)^{-1}, \quad (5)$$

where we have introduced the notation  $x = k_z/k$ . The exact Green's function is of the form

$$G(\mathbf{k}) = (\mu + s k^2 + \lambda x^2 + \Sigma(\mu, T, \mathbf{k}))^{-1}, \quad (6)$$

where  $\Sigma(\mu, T, \mathbf{k})$  is equal to a sum of diagrams, the simplest of which are presented in Fig. 1.

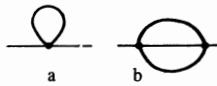


FIG. 1

At the second-order transition point  $G(0) = \infty$  and the transition temperature is determined by the equation

$$\mu + \Sigma(\mu, T_c, 0) = 0. \tag{7}$$

The term described by the diagram 1a does not depend on  $k$  and is equal to

$$\Sigma_1 = \frac{Tbv_{un}}{2} \int \frac{dk}{(2\pi)^3} G(k). \tag{8}$$

Let us expand this expression near the transition point in a series in powers of  $\mu + \Sigma$  and substitute in (6). As a result we obtain

$$G(k) = \left[ sk^2 + \lambda x^2 + (\mu + \Sigma_{10}) \left( 1 + \gamma \ln \frac{\Lambda}{\mu + \Sigma} \right) \right]^{-1}, \tag{9}$$

where

$$\Lambda = \min\{\lambda; s/a^2\}, \quad \gamma = T_c bv_n / 32\pi\sqrt{\lambda s^3}, \tag{10}$$

$$\Sigma_{10} = \frac{Tbv_{un}}{2} \int \frac{dk}{(2\pi)^3} \frac{1}{sk^2 + \lambda x^2}. \tag{11}$$

Large  $k$  are important in the latter integral and expression (11) can therefore only be used for estimates. It should at the same time be noted that the contribution of the interaction of the critical phonons with other branches to  $\Sigma_{10}$  is of the same order of magnitude as the integral of (11).

The dimensionless quantity  $\gamma$  is proportional to the anharmonic interaction constant of the phonons, and is small compared to unity in displacement-type transitions. Therefore at temperatures not too close to  $T_C$  the term with the logarithm in the denominator of (9) is small. Neglecting it and substituting in place of  $\Sigma_{10}$  expression (11), we obtain for the dielectric permittivity the Curie-Weiss law

$$\varepsilon = \lambda G(0) = C_+ / (T - T_c), \tag{12}$$

where

$$C_+ = T\lambda / \Sigma_{10}. \tag{13}$$

Near  $T_C$  even for  $\gamma \ll 1$  the term  $\gamma \ln [\Lambda / (\mu + \Sigma)]$  is not small. In this case one must not restrict oneself only to diagram 1a. For example, diagram 1b corresponds to

$$\Sigma_2 = \Sigma_{20} + 2(\Sigma + \mu) \left( \gamma \ln \frac{\Lambda}{\mu + \Sigma} \right)^2 + \frac{1}{2} k^2 \gamma^2 \ln \frac{\Lambda}{\mu + \Sigma}. \tag{14}$$

The last term leads to a renormalization of  $s$  in the expression for the Green's function. This term, as well as the contributions of higher orders, is proportional to  $\gamma (\gamma \ln (\Lambda / (\mu + \Sigma)))^n$  and is therefore small for  $\gamma \ln (\Lambda / (\mu + \Sigma)) \lesssim 1$ . As is shown in Appendix 1, the renormalization of  $s$  is small for arbitrary logarithms.

The second term, as well as the corresponding first-order term, is proportional to  $[\gamma \ln (\Lambda / (\mu + \Sigma))]^n$ . Summing terms of such order, we obtain for the Green's function for  $T > T_C$  the expression

$$G(k) = (m + sk^2 + \lambda x^2)^{-1},$$

where  $m = \mu + \Sigma(\mu, T, 0)$  and vanishes at the transition point.

### 3. SCATTERING AMPLITUDE OF THE PHONONS

In the first order in the anharmonicity the dimensionless scattering amplitude is the quantity  $\gamma$ . In the following orders of perturbation theory the amplitude is depicted by diagrams, a part of which is shown in Fig.

2. The diagrams 2a, b, and c give contributions proportional to  $\gamma (\gamma \ln (\Lambda / (m + sk^2)))^n$  ( $n$  is the order of perturbation theory) and the diagram 2d is proportional to  $\gamma^4 \ln (\Lambda / (m + sk^2))$ . In the accepted "parquet" approximation one takes into account diagrams of the type 2a, b, and c, and one ignores the contribution of diagrams of the type 2d.

When the momenta entering are of the same order of magnitude and  $sk^2 \gg m$ , then the amplitude  $\Gamma$  depends only on one variable  $y = \ln (sk^2/m)$ . In order to sum the "parquet" diagrams we use the method of [5]. Any "parquet" diagram can be divided into two parts by cutting only two lines. In those instances in which this can be done in several ways, as for example in Fig. 2c, we cut at the place where the momentum  $p$  over which the integration is carried out has a minimum. One then has at the right and at the left of the section diagrams which yield after summation total amplitudes  $\Gamma$ . However, in the expressions corresponding to these diagrams the integration is over momenta greater than  $p$ . Within the logarithmic accuracy under consideration the dependence of the amplitude  $\Gamma$  on the external momenta is determined by the limits of integration over the intermediate momenta. Therefore the sums of the diagrams on the right and on the left from the section are equal to the scattering amplitude of phonons whose momenta are all of the same order of magnitude  $p$ . As a result one obtains the equation

$$\Gamma(k) = \gamma - 3 \frac{8\sqrt{\lambda s^3}}{\pi} \int_{[(sk^2+m)/s]^{1/2}}^{(\Lambda/s)^{1/2}} \Gamma^2(p) \frac{p^2 dp dx}{(\lambda x^2 + sp^2)^2}. \tag{16}$$

The factor 3 is equal to the number of combinations by means of which the four ends of the amplitudes can be divided into two. Going over to the logarithmic variables  $y = \ln (sk^2/m)$  and  $L = \ln (\Lambda/m)$  and differentiating over  $y$  we obtain the equation

$$d\Gamma / dy = 3\Gamma^2(y). \tag{17}$$

The solution of Eq. (17) which satisfies the boundary condition  $\Gamma(L) = \gamma$  is of the form

$$\Gamma(k^2) = \gamma \left/ \left[ 1 + 3\gamma \ln \frac{\Lambda}{sk^2 + m} \right] \right. \tag{18}$$

It is seen from (18) that the effective interaction  $\Gamma$  for appreciable  $sk^2 \cong m$  tends to zero on approaching the transition point.

In obtaining formula (18) we summed only over "parquet" diagrams. In particular, in the expression for the amplitude we neglected diagram 2d which is proportional to  $\gamma^4 \ln (\Lambda / (sk^2 + m))$ . Near the transition point when  $\gamma^3 \ln^2 (\Lambda/m) \gtrsim 1$  the contribution of this expression compared with the obtained expression (18) is

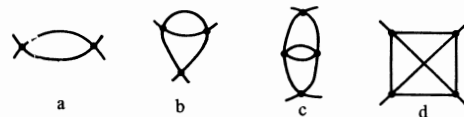


FIG. 2

not small. However, an account of more complicated diagrams leads to the replacement of the bare amplitudes  $\gamma$  by total amplitudes  $\Gamma$ , after which the contribution of the diagrams 2d as well as that of other "non-parquet" diagrams turns out to be small.

#### 4. THE SUSCEPTIBILITY AND SPECIFIC HEAT ABOVE THE TRANSITION POINT

The temperature dependence of the susceptibility is determined by the behavior of the Green's function for  $k = 0$ . In the intermediate formulas it turns out to be convenient to find the dependence of  $G$  on the parameter  $\mu$  with the temperature fixed. Following this, one can find the temperature dependence of the individual parts with the aid of the relation

$$T - T_c = (\mu - \mu_c) \frac{\partial T_c}{\partial \mu}. \quad (19)$$

The derivative  $\partial T_c / \partial \mu$  is determined from Eq. (7) and  $\mu_c$  from the equation

$$\mu_c + \Sigma(\mu_c, T, 0) = 0. \quad (20)$$

In order to determine the dependence of  $G(0)$  on  $\mu$  we make use of Ward's identity

$$\frac{\partial G^{-1}(0)}{\partial \mu} = \mathcal{F}(0, 0, 0), \quad (21)$$

where  $\mathcal{F}$  is the vertex part which is represented by diagrams with two ends and one angle. In the case in which all three momenta on which  $\mathcal{F}$  depends are of the same order  $k$ , the equation for  $\mathcal{F}$  can be obtained in the same way as Eq. (16) for the amplitude:

$$\mathcal{F}(k) = 1 - \frac{8\sqrt{\lambda s^3}}{\pi} \int_{[(sk^2+m)/s]^{1/2}}^{(\Lambda/s)^{1/2}} \mathcal{F}(p) \Gamma(p) \frac{p^2 dp dx}{(\lambda x^2 + sk^2)^2}. \quad (22)$$

Going over to logarithmic variables and substituting for  $\Gamma(p)$  expression (18), we obtain

$$\mathcal{F}(y) = [1 + 3\gamma(L - y)]^{-1/2}. \quad (23)$$

Thus, Eq. (21) takes on the form

$$\frac{dm}{d\mu} = \left(1 + 3\gamma \ln \frac{\Lambda}{\mu - \mu_c}\right)^{-1/2}. \quad (24)$$

Solving this equation with logarithmic accuracy, we obtain

$$m = (\mu - \mu_c) \left(1 + 3\gamma \ln \frac{\Lambda}{\mu - \mu_c}\right)^{-1/2}. \quad (25)$$

As a result we obtain for the susceptibility, instead of (12), the expression

$$\varepsilon = \frac{C_+}{T - T_c} \left[1 + 3\gamma \ln \left(\frac{\Lambda}{\lambda} \frac{C_+}{T - T_c}\right)\right]^{1/2}. \quad (26)$$

Thus the susceptibility tends to infinity somewhat more rapidly than in accordance with the Curie-Weiss law.

The singular part of the specific heat is conveniently evaluated with the aid of the expression

$$C = -T_c \left(\frac{\partial T_c}{\partial \mu}\right)^{-2} \frac{\partial^2 F}{\partial \mu^2} = -T_c \left(\frac{\partial T_c}{\partial \mu}\right)^{-2} \Pi. \quad (27)$$

The polarization operator  $\Pi$  is represented by the aggregate of all diagrams with two angles. As in the derivation of expression (16), we carry out the cutting of any diagram along the two lines with the smallest

momenta. As a result we obtain

$$\Pi = \frac{1}{(2\pi)^2} \int \mathcal{F}^2(k) \frac{k^2 dk dx}{(\lambda x^2 + sk^2 + m)^2}. \quad (28)$$

Substituting expression (22) for  $\mathcal{F}$  and integrating over the logarithmic variables, we obtain

$$\Pi = -\frac{1}{16\pi\gamma\sqrt{\lambda s^3}} \left[ \left(1 + 3\gamma \ln \frac{\Lambda}{m}\right)^{1/2} - 1 \right]. \quad (29)$$

The same expression can be obtained from the usual equation  $\Pi = GG + GG\Gamma GG$ . Here one must take into account that for unequal incoming momenta  $\Gamma$  also depends on their ratio and is not equal to expression (18).

Utilizing formulas (27) and (29), we obtain for the specific heat the expression

$$C = \frac{T_c^2}{16\pi\gamma\sqrt{\lambda s^3}} \left(\frac{\partial T_c}{\partial \mu}\right)^{-2} \left[ \left(1 + 3\gamma \ln \frac{\Lambda}{m}\right)^{1/2} - 1 \right]. \quad (30)$$

In the immediate vicinity of the transition point the specific heat per unit volume increases like

$$C = \frac{3^{1/2}}{16\pi\gamma^{1/2}} \left(\frac{T_c}{C_T}\right)^2 \left(\frac{\lambda}{s}\right)^{1/2} \ln^{1/2} \left(\frac{\Lambda}{\lambda} \frac{C_+}{T - T_c}\right). \quad (31)$$

The obtained expression represents the singular part of the specific heat. In the classical region under consideration the nonsingular part follows the law of Dulong and Petit.

#### 5. THE THERMODYNAMICS IN A STRONG ELECTRIC FIELD AND BELOW THE TRANSITION POINT

In an electric field one must add to the Hamiltonian (2) the term  $-Ee_{\text{eff}}\Sigma \xi_1$ . With this there appears a macroscopic dipole moment. A macroscopic moment also appears below the transition point, even in the absence of a field. In this case it is convenient in calculating the statistical averages, as in the theory of the Bose gas, to separate in the Hamiltonian terms containing  $\xi_0$ . The quantity  $\xi_0$  can be considered a parameter and after calculating the thermodynamic functions one can find it from the condition

$$\frac{\partial F}{\partial \xi_0} = \left\langle \frac{\partial H}{\partial \xi_0} \right\rangle = 0. \quad (32)$$

In order to find the temperature dependence of  $\xi_0$ , let us consider the diagrams for the free energy  $F$  as functions of the parameter  $\xi_0$ . Comparing these diagrams with those of the eigen-energy  $\Sigma$ , one can convince oneself that the relation

$$\partial^2 F / \partial \xi_0^2 = G^{-1}(0) \quad (33)$$

is fulfilled. The dependence of  $G(0)$  on  $\mu$  is determined as before by Ward's identity (21) and the dependence on  $\xi_0$  by the equation

$$\frac{\partial^2}{\partial \xi_0^2} G^{-1}(0) = \frac{32\pi}{VT_c} \sqrt{\lambda s^3} \Gamma(m). \quad (34)$$

In the approximation of the higher-order logarithm under consideration the amplitude  $\Gamma$  and the vertex part  $T$  are described by the same diagrams as above the transition point. Therefore they are determined as functions of the parameter  $m = G^{-1}(0)$  as before by formulas (18) and (23).

The additional diagrams appearing below the transition point contain fewer Green's functions and integra-

tions than the parquet diagrams of the same order. The expressions corresponding to these additional diagrams in the asymptotic region are small in their exponent, and for  $sk^2 \sim m$  they are proportional to a smaller power of the logarithm than the expressions corresponding to parquet diagrams of the same order.

Integrating (23), (33) and (34) with logarithmic accuracy and taking into account the relation

$$\left. \frac{\partial F}{\partial \xi_0} \right|_{\xi_0=0} = -e_{\text{eff}} N^{1/2} E,$$

we obtain after substitution in (32) for the parameters  $m$  and  $\xi_0$  the system of equations

$$m = (\mu - \mu_c) \mathcal{F}(m) + \frac{16\pi}{VT_c} \sqrt{\lambda s^3} \Gamma(m) \xi_0^2, \quad (35)$$

$$-e_{\text{eff}} N^{1/2} E + (\mu - \mu_c) \mathcal{F}(m) \xi_0 + \frac{32\pi}{6VT_c} \sqrt{\lambda s^3} \Gamma(m) \xi_0^3 = 0. \quad (36)$$

Solving this system for  $E = 0$  below the transition point, we find for the spontaneous polarization and for the permittivity the relations

$$P_0^2 = \frac{3}{64\pi^2 \gamma} \left( \frac{T_c}{C_+} \right) \left( \frac{\lambda}{s} \right)^{3/2} \left[ 1 + 3\gamma \ln \frac{\lambda}{\lambda} \frac{C_+}{T_c - T} \right]^{3/2} (T_c - T), \quad (37)$$

$$\epsilon = \frac{1}{2} \frac{C_+}{T_c - T} \left( 1 + 3\gamma \ln \frac{\lambda}{\lambda} \frac{C_+}{T_c - T} \right)^{1/2}. \quad (38)$$

It is clear from the obtained expressions that the spontaneous polarization vanishes somewhat more slowly than in the phenomenological theory and the dielectric increases more rapidly, the "law of two" being fulfilled—the permittivity below the transition point being smaller by a factor of two than the permittivity above the point for the same  $|T - T_c|$ .

In a strong field one can neglect the second term in (36); this yields

$$P^3 = \frac{3}{(4\pi)^3 \gamma} \left( \frac{\lambda}{s} \right)^{3/2} T_c E \left( 1 + 3\gamma \ln \frac{\lambda E}{\lambda} \right), \quad (39)$$

$$\epsilon = 3^{-3/2} \left( \frac{\lambda}{s} \right)^{1/2} \frac{T_c^{1/2}}{\gamma^{1/2} E^{1/2}} \left( 1 + 3\gamma \ln \frac{\lambda E}{\lambda} \right)^{1/2}. \quad (40)$$

In order to calculate the specific heat in a field and below the transition point, one must take into account that not only the zeroth Green's functions but also the spontaneous moment  $\xi_0$  depends on the parameter  $\mu$ . After differentiation and taking into account (32) we obtain for a constant acting field

$$\frac{\partial^2 F}{d\mu^2} = F_{\mu\mu} - \frac{(F_{\mu\xi})^2}{F_{\xi\xi}}. \quad (41)$$

The first term in the right-hand part of (41) is expressed as previously in terms of the polarization operator and the second term can be found by using (36) and (33). Substituting (41) in (27), we obtain

$$C = \frac{1}{16\pi\gamma} \left( \frac{T_c}{C_+} \right)^2 \left( \frac{\lambda}{s} \right)^{3/2} \left[ 4 \left( 1 + 3\gamma \ln \frac{\lambda}{\lambda} \frac{C_+}{T_c - T} \right)^{1/2} - 1 \right]. \quad (42)$$

At temperatures not too close to the transition point (42) gives a constant equal to the jump of the specific heat in the phenomenological theory. Near the transition point the specific heat increases in accordance with the same law as above the transition point.

## 6. GENERALIZATION OF THE MODEL

Above we have considered a model with a weak phonon interaction. The obtained expressions represent the first term of an expansion in the "physical charge"

$\gamma_c = \Gamma(sk^2 \sim m)$ . Expression (18) shows that in the limit  $m \rightarrow 0$  the charge  $\gamma_c$  tends to zero and is independent of the bare interaction  $\gamma$ . It can be expected that the nature of the solutions does not change essentially on going over from small to large  $\gamma$ . We shall therefore assume that  $\gamma_c \ll 1$  for sufficiently small  $m$ . There exists then a region  $sk^2 \gg m$  for which  $\Gamma(k^2) \ll 1$ . We shall therefore choose  $m \ll \Lambda \ll s/a^2$  so that  $\Gamma(\Lambda) = \gamma \ll 1$ . If in evaluating the integrals in the terms of the perturbation theory series one first carries out the integration over  $k^2 > \Lambda/s$ , then one obtains a series in  $\gamma$ . Integration over  $k^2 < \Lambda/s$  leads to formula (18).

The quantity  $\gamma$  does not depend on the temperature. In the case of strong coupling  $\gamma$  is not expressed in terms of the constant of the Hamiltonian in accordance with (10) and can be considered to be a phenomenological parameter. Other parameters are  $s$ ,  $T_c$ , and  $\partial T_c / \partial \mu$ . A temperature dependence of  $\Gamma(k^2)$  appears for  $sk^2 \lesssim m$  and is determined by Eq. (18). All the other quantities have analogously the same temperature dependence as in the case of weak coupling.

The case in which the obtained results go over continuously into the results of the phenomenological theory and which therefore requires no additional assumptions occurs not only for small anharmonicity but also in the case of a large interaction radius  $V_{ij}$  for anharmonicity of arbitrary magnitude. The corresponding diagram technique is described in<sup>13</sup>. In addition to the usual four-phonon interaction there appear in this case interactions of six, etc. phonons. However the contribution of such interactions, which is insensitive to the region of small momenta, does not change the temperature dependences.

In the limit of large anharmonicity the Hamiltonian (2) goes over into the Hamiltonian of the Ising model. For a large interaction radius the effective bare amplitude  $\gamma \sim r_0^{-3}$  is in this model small. In the nearest-neighbor interaction there is no small parameter and the obtained results are only valid when an additional assumption concerning the field of the charge is fulfilled.

In the case of a weak dipole-dipole interaction there exists a large temperature range, not too close to the transition, within which this interaction is unimportant. However, sufficiently close to the transition point when  $m \ll \lambda$  the situation becomes logarithmic. With this  $\Gamma(\lambda) \sim 1$  and the results obtained are applicable with the same stipulations as in the case of strong coupling.

The opposite situation occurs when the ferroelectric is a semiconductor. In this case at distances greater than the Debye radius the dipole-dipole interaction is screened by free carriers. Therefore the formulas obtained above are correct at temperatures not too close to the transition point when the correlation radius is smaller than the Debye radius.

No account was taken above of the interaction of critical phonons and acoustic phonons. In the elastic isotropic model such an interaction leads to the transition becoming a first-order transition.<sup>19</sup> If the striction is small, then the temperature hysteresis is exponentially small and the results obtained above are valid in a broad temperature range. Acoustic and optic phonons with wave vectors lying in the basal plane are important in the uniaxial case. For these wave vectors a crystal with hexagonal symmetry is equivalent to an

isotropic solid and for such crystals the entire thermodynamics is determined by the general formulas of<sup>[9]</sup> in which one must substitute the expression for the specific heat without account of the interaction with acoustic phonons (30) and (42).

## 7. CONCLUSION

The results obtained show that the phase transition in uniaxial ferroelectrics has a series of features due to the presence of a dipole-dipole interaction. The dependences of the thermodynamic quantities differ in this case weakly (logarithmically) from the dependences predicted by the phenomenological theory. In displacement-type transitions when the bare interaction constant  $\gamma$  is small deviations from the phenomenological theory appear in the region exponentially close to the transition point. For order-disorder type transitions where there is apparently no small parameter one can use near the transition point the asymptotic limits. In this case the specific heat increases as  $\ln^{1/3} |T - T_C|$ , the coefficient below the transition point  $T_C$  being larger by a factor of four than above  $T_C$  for a zero acting field and the same as above  $T_C$  for constant induction. The susceptibility is proportional to  $|T - T_C|^{-1} \ln^{1/3} |T - T_C|$ , the "law of two" being fulfilled; the spontaneous polarization vanishes as  $(T_C - T)^{1/2} \ln^{1/3} (T_C - T)$ . Such results are in qualitative agreement with experiment. Thus in triglycine sulphate<sup>[10]</sup> and in  $\text{RbH}_2\text{PO}_4$ <sup>[11]</sup> the specific heat increases in accordance with a close-to-logarithmic law, and for the susceptibility the deviations from the Curie-Weiss law are small.

The obtained results are apparently applicable to transitions in uniaxial ferromagnets; however, the magnetic dipole-dipole forces are usually small compared with the exchange interaction. Therefore the formulas obtained above are only applicable in a narrow region near the transition point. This explains possibly the behavior of the magnetization of nickel which decreases at temperatures  $0.88 T_C < T < 0.99 T_C$  like  $(T_C - T)^{1/3}$  and for  $T > 0.99 T_C$  like  $(T_C - T)^{1/2}$ .<sup>[12]</sup>

A detailed experimental investigation of the features of the thermodynamic quantities in uniaxial ferroelectrics would be of interest not only for the physics of phase transitions but also for checking the general methods of quantum field theory. For the same reasons it is interesting to carry out numerical calculations of the Ising model with a dipole-dipole interaction and for the four-dimensional models discussed in Appendix 2.

## APPENDIX 1

A convenient method of constructing successive approximations in the parameter

$$\gamma_c = \Gamma(sk^2 \sim m) \quad (\text{A1.1})$$

is the method of the renormalization group.<sup>[12]</sup>

An analysis of the perturbation-theory diagrams shows that the theory under consideration has the property of renormalizability, i.e. the dependence of all quantities on the cut-off parameter  $\Lambda$  can be eliminated by the introduction of a "physical" charge  $\gamma_c$  and renormalization factors which do not depend on the momentum  $k$ . Thus, one can write for the amplitude

$$\Gamma(sk^2) = \frac{\Gamma_c(\gamma_c, sk^2)}{\Gamma_c(\gamma_c, \Lambda)} \gamma. \quad (\text{A1.2})$$

[Usually one chooses  $\Gamma_c(\gamma_c \Lambda) = \gamma$ .] In order to find the dependence of  $\Gamma_c$  on  $\Lambda$ , we shall assume that  $\gamma$  depends on  $\Lambda$  in such a way that  $\gamma_c$  remains fixed. If we now choose  $sk^2$  close to  $\Lambda$  and use first-order perturbation theory, then we obtain

$$\Gamma_c(\gamma_c, \Lambda) \left( 1 - 3\gamma \ln \frac{\Lambda}{sk^2} \right) = \Gamma_c(\gamma_c, sk^2). \quad (\text{A1.3})$$

Expressing  $\gamma$  in terms of  $\gamma_c = \Gamma(m)$  with the aid of expression (A1.2) and making in (A1.3)  $sk^2$  tend towards  $\Lambda$ , we obtain the equation

$$\Lambda \frac{\partial \Gamma_c(\gamma_c, \Lambda)}{\partial \Lambda} = 3\gamma_c \frac{\Gamma_c^2(\gamma_c, \Lambda)}{\Gamma_c(\gamma_c, m)}, \quad (\text{A1.4})$$

whose solution is of the form

$$\Gamma_c(\gamma_c, \Lambda) = \frac{\Gamma_c(\gamma_c, m)}{1 - 3\gamma_c \ln(\Lambda/m)}. \quad (\text{A1.5})$$

Substituting this expression in (A1.2) with account of (A1.1), we obtain

$$\gamma_c = \frac{\gamma}{1 + 3\gamma \ln(\Lambda/m)}, \quad (\text{A1.6})$$

$$\Gamma(sk^2) = \gamma \left[ 1 + 3\gamma \ln \frac{\Lambda}{sk^2 + m} \right].$$

The latter formula coincides with (18) obtained by summing higher-order logarithms.

In the asymptotic region the Green's function is of the form

$$G(k) = (sk^2 + \lambda x^2)^{-1}. \quad (\text{A1.7})$$

We note that the parameter  $\lambda$  is not renormalized and the renormalization of the parameter  $s$  in second-order perturbation theory is given by (14). In order to obtain an expression valid for  $\gamma \ln(\Lambda/sk^2) \gtrsim 1$ , we make again use of the renormalizability

$$s(sk^2) = \frac{s_c(sk^2, \gamma_c)}{s_c(\Lambda, \gamma_c)} s. \quad (\text{A1.8})$$

As was done above in seeking the amplitude, using the result of perturbation theory, we obtain

$$\Lambda \frac{\partial s_c}{\partial \Lambda} = \frac{1}{2} \gamma_c^2 s_c \left( 1 - 3\gamma_c \ln \frac{\Lambda}{m} \right)^{-2}. \quad (\text{A1.9})$$

Solving this equation and substituting the obtained solution in (A1.8), we obtain with account of (A1.6)

$$s_c(sk^2) = s \left[ 1 + \frac{1}{2} \gamma_c^2 \left( 1 + 3\gamma \ln \frac{\Lambda}{sk^2 + m} \right)^{-1} \ln \frac{\Lambda}{sk^2 + m} \right] \quad (\text{A1.10})$$

This expression is of the same form as the renormalization of the Green's function of the electron in quantum electrodynamics.<sup>[14]</sup>

It is seen from (A1.10) that the renormalization of the  $s$  parameter is also small for large logarithms.

## APPENDIX 2

As has been noted, the problem of the phase transition in a uniaxial ferroelectric which has been considered is equivalent to the problem of the phase transition in the four-dimensional model with one real field.

It turns out that the form of the singularity depends on the symmetry of the Hamiltonian. In order to explain this dependence we consider a four-dimensional

model with  $n$  real fields. The Hamiltonian of such a model is of the form

$$H = \frac{1}{2} \sum_i \mu \xi_i^\alpha \xi_i^\alpha + \frac{1}{2} \sum_{ij} V_{ij} (\xi_i^\alpha - \xi_j^\alpha)^2 + \frac{b}{4!} \sum_i (\xi_i^\alpha \xi_i^\alpha)^2. \quad (\text{A2.1})$$

The case of two real fields is equivalent to one complex field and corresponds to the Bose-Einstein condensation of a four-dimensional Bose gas.

Repeating the derivation of formulas (16) and (22), we obtain equations for the amplitude and the vertex

$$\Gamma_{\alpha\beta\mu\nu}(x) = \gamma(\delta_{\alpha\beta}\delta_{\mu\nu} + \delta_{\alpha\nu}\delta_{\beta\mu} + \delta_{\alpha\mu}\delta_{\beta\nu}) - \int_x^L dy \{ \Gamma_{\alpha\beta\sigma\rho}(y) \Gamma_{\sigma\rho\mu\nu}(y) + \Gamma_{\alpha\sigma\beta\rho}(y) \Gamma_{\sigma\rho\mu\nu}(y) + \Gamma_{\alpha\sigma\rho\beta}(y) \Gamma_{\sigma\mu\nu\rho}(y) \},$$

$$\mathcal{F}_{\alpha\beta}(x) = \delta_{\alpha\beta} - \int_x^L dy \mathcal{F}_{\mu\nu}(y) \Gamma_{\mu\nu\alpha\beta}(y). \quad (\text{A2.2})$$

It follows from symmetry considerations that  $\Gamma_{\alpha\beta\mu\nu} = \Gamma\{\delta_{\alpha\beta}\delta_{\mu\nu} + \delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}\}$  and  $\mathcal{F}_{\alpha\beta} = \mathcal{F}\delta_{\alpha\beta}$ . Substituting these expressions in Eq. (A2.2), we obtain the equations

$$\Gamma(x) = \gamma - (n+8) \int_x^L dy \Gamma^2(y), \quad (\text{A2.3})$$

$$\mathcal{F}(x) = 1 - (n+2) \int_x^L dy \Gamma(y) \mathcal{F}(y),$$

the solutions of which are of the form

$$\Gamma(x) = \frac{\gamma}{1 + \gamma(n+8)(L-x)}, \quad (\text{A2.4})$$

$$\mathcal{F}(x) = [1 + \gamma(n+8)(L-x)]^{-(n+2)/(n+8)}. \quad (\text{A2.5})$$

Making use of (28), we calculate the polarization operator

$$\Pi = - \frac{1}{(4\pi)^2 \gamma(4-n)} \left\{ \left[ 1 + \gamma(n+8) \ln \frac{\Lambda}{m} \right]^{(4-n)/(n+8)} - 1 \right\}. \quad (\text{A2.6})$$

Substituting the obtained expressions (A2.6), (A2.5), and (A2.4) in (26), (30), and (37), we obtain the main thermodynamic dependences which in the asymptotic region

$$\gamma \ln \frac{C_+}{|T - T_c|} \gg 1$$

are of the form

$$C \sim \ln^{(4-n)/(n+8)} \frac{C_+}{|T - T_c|} \quad (n < 4); \quad C \sim \ln \ln \frac{C_+}{|T - T_c|} \quad (n = 4),$$

$$\varepsilon \sim |T - T_c|^{-1} \ln^{(n+2)/(n+8)} \frac{C_+}{|T - T_c|},$$

$$P\phi^2 \sim (T_c - T)^{1/2} \ln^{6/(n+8)} \frac{C_+}{|T - T_c|}. \quad (\text{A2.7})$$

For  $n > 4$  the specific heat remains finite and has no jump.

The form of the singularities does not depend on the explicit form of the Hamiltonian and is determined solely by the number of fields. For instance, for a four-dimensional lattice of spins analogous results can be obtained by the methods of<sup>[3,15]</sup>. In the Ising model which corresponds to one real field the specific heat increases as  $\ln^{1/3}|T - T_c|$ .

A Bose gas is equivalent to a lattice of plane dipoles.<sup>[16]</sup> In this case the specific heat increases as  $\ln^{1/6}|T - T_c|$ . Finally, in the four-dimensional Heisenberg model which corresponds to a vector field the specific heat goes as  $\ln^{1/11}|T - T_c|$ , and the form of the singularity does not depend on the magnitude of the spin.

<sup>1</sup>M. A. Krivoglaz, *Fiz. Tverd. Tela* 5, 3437 (1963) [*Sov. Phys.-Solid State* 5, 2526 (1964)].

<sup>2</sup>A. P. Levanyuk, *Izv. AN SSSR, Ser. Fiz.* 29, 879 (1965).

<sup>3</sup>V. G. Vaks, A. I. Larkin, and S. A. Pikin, *Zh. Eksp. Teor. Fiz.* 51, 361 (1966) [*Sov. Phys.-JETP* 24, 240 (1967)].

<sup>4</sup>L. D. Landau, A. A. Abrikosov, and I. M. Khalatnikov, *Dokl. Akad. Nauk SSSR* 95, 497, 773, 1177 (1954).

<sup>5</sup>I. T. Dyatlov, V. V. Sudakov, and K. A. Ter-Martirosyan, *Zh. Eksp. Teor. Fiz.* 32, 767 (1957) [*Sov. Phys.-JETP* 5, 631 (1957)]; V. V. Sudakov, *Dokl. Akad. Nauk SSSR* 111, 338 (1956).

<sup>6</sup>P. W. Anderson, *The Physics of Dielectrics*, (Russ. transl.) AN SSSR, 1960, p. 290.

<sup>7</sup>V. G. Vaks, *Zh. Eksp. Teor. Fiz.* 54, 910 (1968) [*Sov. Phys.-JETP* 27, 486 (1968)].

<sup>8</sup>A. A. Abrikosov, A. P. Gor'kov, and I. E. Dzyaloshinskiĭ, *Metody kvantovoi teorii polya v statisticheskoi fizike* (Methods of Quantum Field Theory in Statistical Physics), Fizmatgiz, 1962 [Prentice-Hall, 1963].

<sup>9</sup>A. I. Larkin and S. A. Pikin, *Zh. Eksp. Teor. Fiz.* 56, 1664 (1969) [*Sov. Phys.-JETP* 29, 888 (1969)].

<sup>10</sup>Brindlay, *Phys. Rev. Letters* 18, 239 (1965) [sic-Tr.]

<sup>11</sup>M. Amin and B. A. Strukov, *Fiz. Tverd. Tela* 10, 3158 (1968) [*Sov. Phys.-Solid State* 10, 2498 (1969)].

<sup>12</sup>Dash, *J. Appl. Phys.* 37, 1175 (1966) [sic!].

<sup>13</sup>N. N. Bogolyubov and D. V. Shirkov, *Teoriya kvantovykh polei* (Quantum Field Theory), Gostekhizdat, 1957.

<sup>14</sup>L. P. Gor'kov, *Dokl. Akad. Nauk SSSR* 105, 65 (1955).

<sup>15</sup>V. G. Vaks, A. I. Larkin, and S. A. Pikin, *Zh. Eksp. Teor. Fiz.* 53, 281 (1967) [*Sov. Phys.-JETP* 26, 188 (1968)].

<sup>16</sup>V. G. Vaks and A. I. Larkin, *Zh. Eksp. Teor. Fiz.* 49, 915 (1965) [*Sov. Phys.-JETP* 22, 678 (1966)].

Translated by Z. Barnea