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CORRELATION EFFECTS IN DISPLACEMENT PHASE TRANSITIONS IN FERROELECTRICS

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It is shown that correlation effects in the region of ferroelectric transitions of the displacement type are apparently not small and can significantly affect the thermodynamics of the transition. The first correlation correction to the free energy and the temperature-dependent corrections to the Devonshire expansion coefficients above the transition are found. The thermodynamics near the transition and in the ferroelectric phase is investigated qualitatively. It is shown that the correlation effects can explain some of the properties of the transitions, particularly the proximity of first-order transitions to those of second-order and the temperature dependence of the Devonshire coefficients. The results are compared with experiments on $BaTiO_3$. Numerical estimates of the temperature anomalies of various quantities near the transition are presented.

1. INTRODUCTION

THE thermodynamics of ferroelectrics of the displacement type is customarily described with the aid of the Devonshire expansion[1] of the free energy in powers of the polarization P and of the temperature T. This expansion is a particular case of the Landau phenomenological theory of phase transitions[2], and for a free crystal it takes the form

$$F(P, T) = {}^1/_2\alpha_0(T - T_c)P^2 + {}^1/_4BP^4 + {}^1/_6cP^6, \qquad (1)$$

where the coefficients α_0, B, and c are assumed to be independent of the temperature T. If $B > 0$, then a second-order transition takes place at $T = T_c$, and the highest-order term cP^6 becomes superfluous, whereas if $B < 0$, then a first-order phase transition occurs at $T = T_0 > T_c$, and the addition of the term with cP^6 is essential for the stability of the system. For a more detailed description of the elastic, striction, and other properties, the expansion of F is written in the form of a series in P and in the deformations $u_{\alpha\beta}$ (see[1] or Eq. (3) below). The aggregate of the results obtained in this case is in qualitative agreement with experiment[1]. There is therefore a widely held opinion that the expansion (1) is valid for the ferroelectrics under consideration and has a physical meaning, and consequently attempts were also made to derive it microscopically[3,4].

However, the accumulation of data on perovskites, which are the most thoroughly investigated ferroelectrics with a displacement-type transition, points to a number of facts which are difficult to explain within the framework of (1), and require additional artificial hypotheses.

1. All the known transitions of the displacement type are of first order, although they are close to second-order transition in the sense that the difference $T_0 - T_c \ll T_0$, and the spontaneous polarization P and the ion displacements Δx in atomic units are quite small. In the expansion (1) this would correspond to a systematically negative B and to just as systematically anomalously large value of c.

2. In contrast to the assumption that the coefficients of (1) are independent of T, measurements of B in $BaTiO_3$ in an interval ~30° above T_0 yielded a rather strong temperature dependence[4,5], approximated by the formula $B(T) \approx B_0[1 - 9(T/T_0 - 1)]$. Attempts to tie in this dependence with the temperature dependence P(T) below T_0 leads to just as sharp a dependence of c on T[6], namely, $(T = c_0[1 - 8(T/T_0 - 1)]$.

The indicated properties of B and c appear to be particularly strange if an attempt is made to derive (1) microscopically, for example by the methods of[3,4]. In accordance with the sense of the expansion (1), the quantities P and T are small parameters, and the expansion is in powers of the ratios of T to the atomic energy $\epsilon_{at} \sim 1$ eV and of the ratios of the displacements Δx to the inter-ion distances a, viz., $F(P, T) = f(\Delta x a^{-1}, T\epsilon_{at}^{-1})$. The ratios $\Delta x/a$ and T/ϵ_{at} are of the order of several hundreds, so that in order for the second and third terms of (1) to be commensurate the parameter c in the corresponding atomic units should be larger by thousands of times than B. The temperature dependence of B and c in the crystal is a result of anharmonic corrections of relative order $T\epsilon_{at}^{-1}$, so that the temperature corrections to B and c should apparently also be smaller by hundreds of times than the values indicated above.

3. In the Devonshire expansion, the elastic moduli c_{ik} in the paraphase (or in the ferroelectric phase at constant P) should not change with T. Experiment indicates apparently that c_{ik} decreases on approaching T_0[1,7] a possible connection of anomalies of this type with the correlation effects in the region of the transition was discussed by Levanyuk[8]).

4. An argument in favor of (1) is frequently assumed to be satisfaction of the Curie-Weiss law $\epsilon(T) = C(T - T_c)^{-1}$ at $T > T_0$. However, this relation was usually verified in a narrow interval of P, on the order of several dozen degrees. In this interval, variation of the parameters C and T_c makes it possible, as will be shown below, to approximate also the more complicated $1/\epsilon(T)$ dependence by a linear one. To describe $\epsilon(T)$ in broader intervals, one uses the formula $\epsilon(T) = \epsilon_L + C(T - T_c)^{-1}$. As noted in[9], the values of ϵ_L obtained in this case turn out to be approximately four times larger than expected from the usual dispersion formula for a crystal (in which account is taken of the presence of the soft Cochran branch of the oscillation[10]); this also calls for an explanation.

These and some other facts suggest that the phenomenological theory for a quantitative description of the transitions of the displacement type may be just as inconvenient as for transitions in magnetic systems of the order-disorder type[11,12]. The general cause for the deviations from this theory are, as is well known, correlation effects and the interaction of critical fluctuations in the transitions[13,11]. In transitions of the displacement type, these effects consist of interactions between phonons of the critical low-lying branches. It is shown in[4] that the correlation parameter $\xi(T)$, which determines the magnitude of the deviations from the predictions of the phenomenological theory, is proportional in these substances to $T\epsilon_{at}^{-1}$, but increases on approaching the transition.

A quantitative estimate has yielded

$$\xi(T) = a\frac{T}{\sqrt{\varepsilon_{aT}(T-T_c)}} \sim \frac{Tb_{11}}{32\pi^3}\frac{\lambda^{3/2}}{s^{3/2}}\sqrt{\frac{C}{T-T_c}} \qquad (2)$$

Here b_{11} is the coefficient of $P^4/4$ in the Devonshire expansion (3), and λ and s determine the spectrum of the critical phonons $\omega_c(k)$ at small values of k; thus, neglecting the anisotropy, $\omega_c^2(k) = \lambda\epsilon^{-1}(T) + k^2 s$. Since no data on the spectra were available at that time, the value of a for $BaTiO_3$ was estimated in[4], from the values of s for $SrTiO_3$[14]. This yielded $a \sim 10^{-2}$ and has made it possible to regard the correlation effects as small. However, the data of Shirane et al.[15], which were published soon thereafter, have shown that s in $BaTiO_3$ is smaller by several dozen times than in $SrTiO_3$, so that $a \sim 1$ and it turns out that $\xi \sim 1$ at $T \sim T_0$. Thus, in the vicinity of the transition the correlation apparently are not small, and, as will be discussed below, it is possible that the transitions occur precisely at such $T - T_c$ that the correlation effects cease to be small. The small magnitude of these effects makes a quantitative description difficult, but a possibility appears of expanding a number of qualitative effects.

Since there are still no microscopic methods for describing the region $\xi \gtrsim 1$, we confine ourselves below to a calculation of the first correlation correction to F, which corresponds at $T > T_0$ to the first approximation in terms of ξ. The results have a quantitative meaning only when $\xi \ll 1$, i.e., not too close to the transition. But since in these substances ξ is apparently not much larger than unity, the results will probably be suitable for a qualitative description and for semiquantitative estimates also at the limit of the employed approximation $\xi \sim 1$.

We use the notation and the results of[4], which is henceforth cited as I. The critical and acoustic coordinates x_c and u will be defined in accordance with[16], in which a connection the constants μ and μ_r of I are set equal to zero.

2. CALCULATION OF THE FIRST CORRELATION CORRECTION TO THE FREE ENERGY

As discussed in[11,4], to find the first correction to F it is necessary to find the irreducible self-energy part Σ of the correlation (Green's) function G in the first order of perturbation theory. Then F is determined by summing all the chains with these Σ, and in accordance with the rules for writing down the diagrams[17], the chain with n blocks Σ is divided by n, so that the sum of the chains is not a geometric progression, but the expansion of the logarithm. Graphically, F and Σ are shown in Fig. 1; just as in I, the crosses with the dashed lines denote the mean values of the coordinate x_c and of the deformation $u_{\alpha\beta}$. In the expression for F and Σ, we have discarded all the terms of higher orders in P and T, since, as noted in the introduction, their addition is apparently both inconsistent and unnecessary.

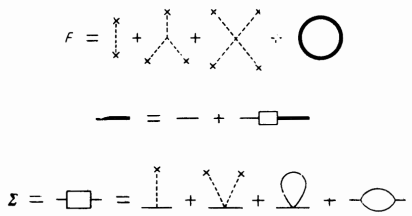

FIG. 1

The analytic expression for F, corresponding to Fig. 1, is

$$\begin{aligned} F - F_0 = {} & \frac{1}{2}c_{\alpha\beta\gamma\delta}u_{\alpha\beta}u_{\gamma\delta} - \gamma T u_{\alpha\alpha} + 2\pi P^2\frac{T-T_{c0}}{C_0} \\ & - q_{\alpha\beta\gamma\delta}P_\alpha P_\beta u_{\gamma\delta} + \frac{b_{11}}{4}\sum_{\sigma=1}^{3}P_\sigma{}^4 + \frac{b_{12}}{2}\sum_{\sigma>\sigma'}P_\sigma{}^2 P_{\sigma'}{}^2 \\ & + \frac{T}{2}\sum_{n=0}^{\infty}\sum_{\mathbf{k}}\mathrm{Sp}\left\{\ln[1+(\Sigma^0+\tilde{\Sigma})G^0] - \Sigma^0 G^0 - \frac{1}{2}(\tilde{\Sigma}G^0)^2\right\}. \end{aligned} \qquad (3)$$

Here F_0 denotes the regular part of F, which does not depend on **P** or $u_{\alpha\beta}$, the first six terms are the Devonshire expansion and are discussed in I, while the last term I_c describes the contribution of the correlation effects. The zeroth Green's function $G^{(0)}(k, i\omega_n)$ is given by expression I(26) at $S_0 = Q = 0$, i.e., it corresponds to neglecting the gap in the spectrum of the critical phonons. In the correlation term I_c, the last two terms in the brackets are subtracted from the first, because their sum $(-\gamma T u_{\alpha\alpha} + 2\pi P^2 T C_0^{-1})$ has already been taken into account in the Devonshire part of F. Since the integral over k in I_c converges at small $k \sim (T - T_c)^{1/2}$ and small P, only the low-frequency critical and acoustic branches are of importance in it, so that G^0_{ij} and Σ^0_{ij} can be taken to mean six-row matrices and their expansion at small k can be employed. In this case $\Sigma^0_{ij} \neq 0$ only when i and j are the critical components; in this case $\Sigma^0_{\alpha\beta} = S^0_{\alpha\beta} = \Sigma^{cc}_{\alpha\beta} + \lambda_c\delta_{\alpha\beta}$, where $\Sigma^{cc}_{\alpha\beta}$ is given by I(24) (with the already mentioned discard of the terms of higher order $\sim TP^2$ and P^4). The components $\tilde{\Sigma}_{\alpha\beta}$ are equal to $Q_{\alpha\beta}$ of I(25) when α and β are the acoustic and critical components, respectively, and are equal to $Q^+_{\alpha\beta}$ when α and β are the critical and acoustic components, respectively; in all other cases they are equal to zero. The expansion of G^0 is

$$(G^0)^{-1} = \begin{pmatrix} A(\mathbf{k}) & V(\mathbf{k}) \\ V(\mathbf{k}) & S(\mathbf{k}) + \lambda g_l \end{pmatrix}. \qquad (4)$$

The matrices A, V, and S, which are proportional to k^2, are determined here by formula I(9), g_l is given by formula I(10); the term λg_l, just as in I(39) and I(30), describes the influence of the Coulomb forces; in the solutions, λ must tend to infinity in accordance with I(30).

We confine ourselves, as before[4,16], to a region of not too low temperatures, $T > \hbar\omega_c(0)$, when in the sum over n in (3) it is sufficient to retain only the term with n = 0, corresponding to the use of classical statistics. Going over from summation over k to integration with respect to $d^3k = k^2dkd\Omega$, integrating over k by parts, and going over from six-row matrices to three-row matrices, we obtain for I_c:

$$I_c = -\frac{T}{3}\int\frac{d\Omega}{(2\pi)^3}\int_0^\infty dk\,\mathrm{Sp}\left[\frac{k^2}{k^2\hat{s} - ik\hat{z} + \sigma + \lambda g_l}\left(\frac{ikz}{2} - \hat{\sigma}\right) + \frac{k^2}{k^2\hat{s} + \lambda g_l}\hat{\sigma} + \frac{1}{2}\left(\frac{k^2}{k^2\hat{s} + \lambda g_l}\hat{z}\right)^2\right].$$

The matrices ŝ, ẑ, and $\hat{\sigma}$, which here no longer depend on k, are defined here by

$$k^2\hat{s} = S - VA^{-1}V, \quad ik\hat{z} = Q^+A^{-1}V + VA^{-1}Q, \quad \hat{\sigma} = S_0 - Q^+A^{-1}Q \quad (5)$$

To effect the transition λ → ∞ it is convenient to change over to a coordinate system in which one of the axes is directed along k, and the other two are perpendicular to it (to the "k-system"). In this system, the transition λ → ∞ in (4) corresponds to retention of only the "transverse" components r_{22}, r_{23}, r_{32}, and r_{33} in all the matrices r_{ik}. In connection with subsequent calculations, we present the explicit form of the matrix of the transition from the system of the crystal axes x, y, z to the k-system, in which the axis 2 lies in the plane (**k**, x):

$$r' = UrU^{-1} = Ur\tilde{U}, \quad U = \begin{pmatrix} n_1 & n_2 & n_3 \\ -n_\perp & n_1n_2/n_\perp & n_1n_3/n_\perp \\ 0 & -n_3/n_\perp & n_2/n_\perp \end{pmatrix}. \quad (6)$$

Here n_i is the projection n = **k**/k on the crystal axis and $n_\perp^2 = 1 - n_i^2$. In the **k**-system, the integration over k is carried out in elementary fashion, and yields

$$I_c = -\frac{T}{48\pi^2}\int d\Omega\,(u_+^{3/2} + u_-^{3/2}), \quad (7)$$

$$u_\pm = \frac{1}{2(s_2s_3 - s_4^2)}\{\sigma_2s_3 + \sigma_3s_2 - 2\sigma_4s_4 - z^2 \pm [(\sigma_2s_3 + \sigma_3s_2 - 2\sigma_4s_4 - z^2)^2 - 4(s_2s_3 - s_4^2)(\sigma_2\sigma_3 - \sigma_4^2)]^{1/2}\},$$

where $r_2 = r_{22}$, $r_3 = r_{33}$, $r_4 = r_{23}$, $z = z_4 = z_{23}$, and the quantities $u_\pm$ depend, generally speaking on **n**.

Formula (7) gives a general expression for the correlation correction for any direction of **P**. To calculate I_c in closed form it is necessary to substitute in (6) the explicit forms of S_0 and Q in accordance with I(24), and I(25), to substitute A, V, and S in accordance with I(9) (for the tetragonal phase, these matrices are given in[18]), and to multiply the matrices.

3. REGION ABOVE THE TRANSITION

Above the transition in not too strong fields, I_c can be expanded in powers of P and $u_{\alpha\beta}$, determining by the same token the correlation corrections to the Devonshire coefficients in (3). In the general case, this yields cumbersome expressions, the presentation of which is meaningful only for numerical calculations. For simplicity and clarity, we neglect the anisotropy of the spectra above the transition, putting in I(9) $a_a = s_a = v_a = 0$, but we retain in the solutions the striction anisotropy $q_a = q_{11} - q_{12} - q_{44}$, so as to show that averaging over the angles in (7) decreases noticeably the contribution of the anisotropy terms, so that in the case of ordinary anisotropy of the order of unity, its influence can be also quantitatively small. Formula (7) for $P = P_x$ takes in this case the form

$$I_c = -\frac{T}{96\pi^{5/2}}\frac{\lambda^{3/2}}{(s_t - v_t^2a_t^{-1})^{3/2}}\int_0^1 dn_1\left\{\left[4\pi\frac{T-T_c}{C} - 2\eta q_+ + 2\zeta q_- + P^2\left(b_{12} - \frac{q_{44}^2}{c_{44}}n_1^2\right)\right]^{3/2} + \left[4\pi\frac{T-T_c}{C} - 2\eta q_+ + 2\zeta q_-(3n_1^2 - 2) + P^2\left(3b_{11}n_\perp^2 + b_{12}n_1^2 - n_1^2\frac{(q_{44} + 2q_\alpha n_\perp^2)^2}{c_{44}} - 4n_\perp^2\frac{(q_{12} + q_0n_1^2)^2}{c_{11}}\right)\right]^{3/2}\right\}, \quad (8)$$

where

$$q_+ = q_{11} + 2q_{12}, \quad q_- = q_{11} - q_{12}, \quad \zeta = \frac{1}{3}\left(u_{11} - \frac{u_{22} + u_{33}}{2}\right),$$
$$\eta = \frac{u_{11} + u_{22} + u_{33}}{3} - \frac{\gamma T}{c_+}, \quad c_+ = c_{11} + 2c_{12},$$
$$\frac{T - T_c}{C} = \frac{T - T_{c0}}{C_0} - \frac{q_+\gamma T}{2\pi c_+}. \quad (9)$$

Substituting (8) in (3) and expanding in powers of P, η, and ζ, we obtain an expression for F above the transition with correlation corrections of first approximation:

$$F - F_0 = -\frac{32\pi^2}{3}\xi\frac{(T-T_c)^2}{b_{11}C^2} + 8\pi\xi\eta q_+\frac{T-T_c}{b_{11}C} + \frac{3}{2}\eta^2c_+\left(1 - \xi\frac{\varkappa_+}{4}\right) + 3\zeta^2c_-\left(1 - \frac{7}{40}\xi\varkappa_-\right) + 2\pi P^2\frac{T-T_c}{C}(1 - \xi a_1) - \eta P^2q_+\left(1 - \xi\frac{a_1}{2}\right) - 2\zeta P^2q_-(1 - \xi a_2) + \frac{b_{11}P^4}{4}(1 - \xi a_3). \quad (10)$$

Here $\xi = \xi(T)$ is given by the right side of (2) with the substitution $s \to s_t - v_t^2a_t^{-1}$, and the constants a_i, $\kappa_\pm$, and c_- are defined by

$$a_1 = 1 + \frac{4\beta - 2q^2 - d^2}{6} - \frac{4\varepsilon q + 2\delta d}{15} - \frac{16\varepsilon^2 + 3\delta^2}{105},$$
$$a_2 = \frac{7}{20} - \frac{7\beta - 2q^2 + 7d^2}{60} - \frac{2\varepsilon q + \delta d}{42} - \frac{12\varepsilon^2 + \delta^2}{315},$$
$$a_3 = \frac{6}{5}\left(1 - \frac{d^2}{3}\right)^2 + \frac{9\beta^2 - 8\beta q^2 + 3q^4}{30} + \frac{1}{5}\left(1 - \frac{d^2}{3}\right)(\beta - q^2) - \frac{8}{35}(2\varepsilon q + \delta d)\left(1 - \frac{d^2}{3} + \frac{\beta - q^2}{4}\right) + \ldots,$$
$$\varkappa_\pm = \frac{4}{3}\frac{q_\pm^2}{b_{11}c_\pm}, \quad c_- = c_{11} - c_{12};$$
$$\beta = \frac{b_{12}}{b_{11}}, \quad q = \frac{q_{44}}{\sqrt{b_{11}c_{44}}}, \quad \varepsilon = \frac{q_a}{\sqrt{b_{11}c_{44}}}, \quad d = \frac{2q_{12}}{\sqrt{b_{11}c_{11}}}, \quad \delta = \frac{2q_a}{\sqrt{b_{11}c_{11}}}. \quad (11)$$

In the formula for a_3 in (11), we have not written out, for the sake of simplicity, the terms of higher order in ϵ and δ, whose coefficients, just as in a_1 and a_2, decrease rapidly with increasing power of ϵ or δ.

The first term of (10) describes the correlation contribution to the specific heat, the second the contribution to the thermal-expansion coefficient, and the next are the corrections to the elastic moduli c_+, to the striction coefficients q_{ik}, and to the nonlinearity b_{11}. The order of magnitude of these corrections and a comparison with experiment on $BaTiO_3$ are discussed in Sec. 6.

4. QUALITATIVE INVESTIGATION OF THE VICINITY OF T_0 IN THE TETRAGONAL PHASE

We start from the assumption[19] that the phase transition in the "clamped" lattice, in which no account is taken of the striction interaction of the critical degrees of freedom with the acoustic ones, is a second-order transition. Then, as shown in[20], the striction interaction causes a first-order transition to occur in the system, and the transition temperature T_0 is determined, rougly speaking, by the condition that the product of the corresponding striction constant by the correlation parameter, which increases on approaching the transition, become of the order of unity. In[20] is considered the case of small striction, when the transition occurs in the region of strong correlation effects, where it is reasonable to describe these effects by dimensional methods[12], and the employed approximation $\xi < 1$ is utterly inapplicable[11]. However, in the ferroelectrics under consideration the striction, generally speaking, is not small, and the parameters $\kappa_\pm$, q, etc. are of the order of unity. It is natural to assume that in this case the transition occurs already at correlation effects on the order of unity, i.e., on the boundary of applicability of the employed approximation $\xi \lesssim 1$. Then we can attempt to employ relations (3) and (8) also for the description of the vicinity of T_0 and of the region above T_0. This can give reasonable qualitative and sometimes, as in the case of "strong striction" described below, also qualitative description of the transition. In addition, its consideration makes it possible to find the natural variables and similarity relations, and also certain inequalities between the thermodynamic coefficients.

We confine ourselves, as above, to the tetragonal case $P = P_x$, and introduce in place of P, T, η, ζ the dimensionless variables x, t, u, and v:

$$b_{11}P_x^2 = \alpha^2 x, \quad \frac{4\pi(T-T_c)}{C} = \alpha^2 t, \quad 2q_+\eta = \alpha^2\left(u + x\frac{\varkappa_+}{2}\right),$$
$$2q_-\zeta = \alpha^2\left(v + x\frac{\varkappa_-}{2}\right); \tag{12}$$

here

$$\alpha = \frac{T}{32\pi^{5/2}}\frac{b_{11}\lambda^{3/2}}{(s_t - v_t^2 a_t^{-1})^{3/2}}.$$

The quantity $\alpha \sim T\epsilon_{at}^{-1} \ll 1$, and the phase transition occurs at $\xi = 2t^{-1/2} \sim 1$, i.e., at $t \sim 1$.

In terms of the variables (12), the dimensionless free energy φ takes the form

$$\varphi = \frac{b_{11}(F-F_0)}{\alpha^4} = \frac{u^2}{2\varkappa_+} + \frac{v^2}{\varkappa_-} + \frac{xt}{2} + \frac{\nu x^2}{4}$$
$$-\frac{1}{3}\int_0^1 dn_1 (t - u + v + bx - xq^2 n_1^2)^{3/2}$$
$$-\frac{1}{3}\int_0^1 dn_1 \{t - u - v(2-3n_1^2) + x[b + cn_\perp^2 - n_1^2(q + 2\varepsilon n_\perp^2)^2$$
$$- n_\perp^2(d + \delta n_1^2)^2]\}^{3/2};$$
$$\nu = 1 - 0.5\varkappa_+ - \varkappa_-, \qquad b = \beta + 0.5(\varkappa_- - \varkappa_+), \qquad c = 3 - \beta - 1.5\varkappa_-. \tag{13}$$

The equilibrium values of u, v, and x are determined by the conditions $\partial\varphi/\partial u = \partial\varphi/\partial v = \partial\varphi/\partial x = 0$. In describing the transition with the aid of (13), we can use the usual consideration concerning the minimum of F. Far from the transition, both when $t \gg 1$ and when $-t \gg 1$ and $x \gg 1$, the term I_c in (13) is small compared with the Devonshire φ_D, but when $t \sim 1$ the presence of I_c is significant and leads, generally speaking, to the appearance of an additional minimum of $\varphi(x, v)$, besides the point $x = v = 0$. If this minimum becomes smaller than $\varphi(0, 0)$ at $t = t_0$, then a first-order transition takes place. Since a test of expression (13) for a minimum is a cumbersome task, we shall illustrate these considerations by analyzing two particular cases of special relations between the constants in (13). As already noted, in the case of the exact description of the correlation effects (and not the model description as in (13)), the second minimum and the first-order transition must apparently take place[20].

1. The case of "strong" striction, $\nu \ll 1$. From the stability of the cubic phase far from the transition it follows that $\nu > 0$; let us consider the case when the sum of the striction constants 0.5 κ_+ and κ_- is close to the maximum value, unity. It is geometrically obvious that in this case the quality $\varphi(0, 0) = \varphi(x, v)$ will be reached already at quite large t and x, whereas u, v $\ll$ x. Therefore, accurate to first order in $\nu \sim t^{-1} \sim x^{-1/2}$, we can write the function φ in the form

$$\varphi = \frac{xt}{2} + \frac{\nu x^2}{4} - \frac{ax^{3/2}}{3} + \left(\frac{u^2}{2\varkappa_+} + \frac{v^2}{\varkappa_-} - b_u(t-u)\sqrt{x} - b_v v\sqrt{x}\right). \tag{14}$$

Here the constants a, b_u, and b_v are obtained in obvious fashion by expanding (13) at large values of x; the term in the parentheses is a small correction of the order of ν to the first three terms, and is given to illustrate the character of the expansion. Confining ourselves to the first term, we find that the transition point t_0 and the x(t) dependence are determined by the relations

$$t_0 = \frac{2a^2}{9\nu}, \quad x_0 = x(t_0) = \frac{4a^2}{9\nu^2}, \quad \sqrt{x} = \frac{3}{4}\sqrt{x_0}\left(1 + \sqrt{1 - \frac{8t}{9t_0}}\right). \tag{15}$$

If we define the "Curie-Weiss" point t_c by the relation $\partial\varphi/\partial x|_{x=v=0} = 0$, then in this case $t_c \sim 1$ and we get $x(t_c)/x_0 \approx 9/4$. Thus, the "strong" striction corresponds to very rapid growth of x below the transition, although it can be shown that the terms of higher order in ν in the expansion, slow down this growth noticeably already at $\nu \sim 0.2-0.3$. We note also that since in this case the correlation parameter $\xi = 2t^{-1/2}$ is still small in the transition region, the employed approximation of the self-consistent field is quantitative, since the "dangerous" region of large correlations is not attained. The term I_c is comparable with the "zeroth" approximation φ_D in (13) only as a result of the special smallness of φ_D, whereas the terms of next higher order in ξ are smaller in terms of the parameter ν.

2. Case of "weak" striction. At a certain ratio of the constants in (13), a case is possible when x and v are small in the transition region: x, v $\ll$ t − u. Thus, if κ_+ in (13) is small, the corresponding condition takes the form

$$\Delta = a_3 - \nu a_1 + \varkappa_- a_2^2(4a_1 - 0{,}7\varkappa_-)^{-1} \ll 1.$$

Since physically this means that the transition is close to a second-order transition and should actually be accompanied by strong correlations, Eqs. (7) and (13) are not quantitative in this case, but make it possible to trace the character of the results obtained in the case that is the opposite of strong striction.

The expansion of φ in this case is in powers of x and v up to third order, and is analogous to the Devonshire expansion (1), but the coefficients depend on t and u. The general formulas are similar to the Devonshire formulas, but are cumbersome, and we confine ourselves to indicating the dependence x(t) in the vicinity of the transition $t - t_c \sim t_0 - t_c \sim \Delta^2 \ll 1$. We have

$$x(t) = \frac{2}{3} x_0 \left[1 + \left(1 - \frac{3}{4} \frac{t - t_c}{t_0 - t_c} \right)^{1/2} \right], \quad x_0 \sim \Delta. \tag{16}$$

In this case the ratio $x(t_c)/x_0 = 4/3$, so that the polarization increases quite slowly with decreasing t. In the intermediate cases of "medium" striction, the dependence x(t) in accordance with (13) has apparently the character intermediate between (15) and (16).

We have used relations (12) above only for a model investigation of F in accordance with formula (13). However, as already noted, the transition region for the considered substances is characterized apparently by the same values of the parameters x, t, u, $v \sim 1$, while the transition temperatures T_0 vary over a wide range for the different substances. Therefore (12) can be regarded as a set of similarity relations, by putting in them $x_0 \sim t_0 \sim u_0 \sim v_0 \sim$ const for different transitions. This leads to certain statements which will be discussed in Sec. 6 below.

5. RHOMBIC AND RHOMBOHEDRAL PHASES

We have considered above the tetragonal phase, in which $\varphi = \varphi_\tau$ was given by (13). Using (7), we can also consider the rhombic ($\varphi = \varphi_r$) and rhombohedral ($\varphi = \varphi_\rho$) phases. We write out first the general expression for the Devonshire part (3) in the notation of (12)

$$\varphi_D = \frac{u^2}{2\varkappa_+} + \frac{3v^2 + w^2}{3\varkappa_-} + \frac{v_4{}^2 + v_5{}^2 + v_6{}^2}{2q^2} + \frac{x + y + z}{2} t + \nu \frac{(x + y + z)^2}{4} + \mu \frac{xy + yz + zx}{2}. \tag{17}$$

Here

$$\mu = 1 - \beta + q^2 - 1{,}5\varkappa_-, \quad \alpha^2 y = b_{11} P_2{}^2, \quad \alpha^2 z = b_{11} P_3{}^2,$$
$$\alpha^2 (w + {}^3/_4 \varkappa_- (y - z)) = q_- (u_{22} - u_{33}), \quad \alpha^2 (v_4 + q^2 \sqrt{yz}) = q_{44} u_{23}, \tag{18}$$

and v_5 and v_6 are obtained from v_4 by cyclic permutation of the indices 1, 2, and 3.

Below the transition point $t = t_D = 0$ we have $\varphi_D < 0$, and the values of φ_D in the different phases are related like

$$\varphi_{D\tau} : \varphi_{Dr} : \varphi_{D\rho} = \frac{1}{\nu} : \frac{1}{\nu - \mu/2} : \frac{1}{\nu - 2\mu/3}. \tag{19}$$

When $\mu > 0$, the minimum of φ_D corresponds to the rhombohedral phase $x = y = z$, and when $\mu < 0$ we have the tetragonal phase $x \neq 0$, $y = z = 0$. Therefore the possible existence of a rhombic phase $x = y \neq 0$, $z = 0$ in this picture is due entirely to correlation effects. When $\mu > 0$ the possibility that the system will go through a tetragonal and (or) rhombic phase before the rhombohedral phase is reached is also connected with the presence of I_c, namely, the correlation effect, as noted above, decreases with increasing distance from T_c, so that the system tends to a minimum of φ_D with decreasing T.

Explicit calculation of φ_r and φ_ρ in the case of small anisotropy ϵ, δ, $1 - \beta \sim 1$ leads to expressions that are more cumbersome than (13). To illustrate the course of φ_τ, φ_r, and φ_ρ with decreasing T, let us consider in (7) the case of small anisotropy ϵ, δ, $1 - \beta \ll 1$, assuming as before that $a_a = s_a = v_a = 0$; then, as can be readily seen, we also have $\mu \ll 1$. Then in the approximation linear in ϵ, δ, and μ it turns out that the following relations hold between the differences $\varphi_{\tau\rho} = \varphi_\tau - \varphi_\rho$ and $\varphi_{r\rho} = \varphi_r - \varphi_\rho$, at the same value of $P^2 = b_{11}{}^{-1} a^2 (x + y + z)$ and at a transverse dielectric constant $\epsilon_\perp^\tau$ in the tetragonal phase:

$$\varphi_{\tau\rho} = 4\varphi_{r\rho}, \quad \varepsilon_\perp{}^\tau = 2\pi \left[\alpha^2 \left(\frac{\partial \varphi_\tau}{\partial y} \right)_{y=0} \right]^{-1} = \frac{2\pi}{\alpha^2 3 (\varphi_\rho - \varphi_\tau)}. \tag{20}$$

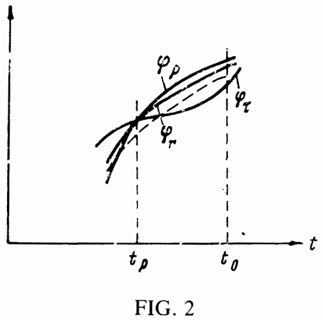

FIG. 2

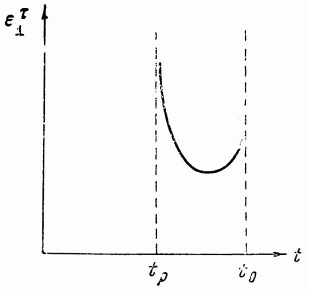

FIG. 3

The differences $\varphi_{\tau\rho}$ and $\varphi_{r\rho}$ are proportional to the anisotropy and to the square of the polarization, so that if P^2 increases below the transition point, then $\varphi_{\tau\rho}$ and $\varphi_{r\rho}$, generally speaking, increase. But if it turns out, for $\mu > 0$, that $\varphi_{\tau\rho}(t_0) < 0$, then, as already noted, the value of $\varphi_{\tau\rho}$ should reverse sign somewhere with decreasing g, and the relative variation of φ_τ, φ_r, φ_ρ and $\epsilon_\perp^\tau$ is as shown in Figs. 2 and 3.

We see that in this approximation, which is linear in the anisotropy, the rhombic phase is missing, as before, but the transition from the tetragonal phase to the rhombohedral phase, accompanied by an increase of $\epsilon_\perp$ (which is infinite in this approximation), is possible. The relations needed for this purpose (which correspond, generally speaking, to smallness of μ), can be obtained by investigating the explicit form of φ_τ and φ_ρ. Thus, in the strong-striction case considered above, $\nu \ll 1$, this condition takes the form

$$0 < \mu < \frac{3A}{2a} \nu, \quad A = \sqrt{2 - d^2} \left(\frac{7}{8} \varepsilon + \frac{\delta}{16} \right) - \frac{3}{4} q \varepsilon. \tag{21}$$

In real substances, the anisotropy is not small, so that the considered approximation, which yields (20), is, in the main, illustrative. In the next-higher approximations in the anisotropy, the relations (20) and the triple intersection of φ_τ, φ_r and φ_ρ at one point, shown in Fig. 2, do not take place. If as a result of this "splitting" the course of φ_r relative to φ_ρ and φ_τ is of the form shown dashed in Fig. 2, then we go through all three phases in succession with decreasing t, namely $\tau \rightarrow r \rightarrow \rho$, and the value of $\epsilon_\perp$ is finite at the point of the second transition.

6. DISCUSSION AND COMPARISON WITH EXPERIMENT

In connection with the noted difficulties of the quantitative description, the most reliable results in the present analysis are the qualitative ones; let us compare them with experiment. From the fact that in the given substances the effective striction constants $\kappa_\pm$, q, ϵ, δ and the correlation effects in the transition region are of the order of unity, it follows, in accordance with Sec. 4, that the transitions should be of first order. Further, we can explain the basic fact, namely the closeness of the transitions to those of second order, namely, according to (12), the values of $\xi(T) = \xi(T_0) \sim 1$ at which the transition takes place, correspond to

$$(T_0 - T_c)\,/\,T_0 \sim T_0\,/\,\varepsilon_{\text{aт}} \ll 1. \qquad (22)$$

If it is assumed that the microparameters of the substances under consideration (particularly perovskites), $\kappa_\pm$, αT^{-1}, etc., which enter in (12) and (17), are of the same order of magnitude, namely atomic, then, according to (12), a systematic growth of the quantities $T_0 - T_c$, $P(T_0)$, $\zeta(T_0)$, etc. should be observed with increasing T_0. A comparison of the data on $BaTiO_3$ ($T_0 \sim 400°$), $KNbO_3$ ($T_0 \sim 700°$), and $PbTiO_3$ ($T_0 \sim 760°$) confirms this tendency. The correlation effects lead to a temperature dependence of the thermodynamic coefficients in the vicinity of the transition; at small values of ξ, it is given by (10). We see that the elastic moduli $c_\pm(T)$ and the nonlinearity coefficient $b_{11}(T)$ decrease, and the change of b_{11} (with allowance for $\nu = 1 - 0.5\kappa_+ - \kappa_- > 0$) is much stronger than for c_+. In the dielectric constant, the approximation of the relation $\epsilon^{-1} = T(T - T_c)C^{-1}(1 - \xi a_1)$ by the formula $\epsilon = \epsilon_L + C_e(T - T_{ce})^{-1}$ leads to the need for introducing a large ϵ_L. Thus, the facts indicated in the introduction find a natural explanation.

The aforementioned "dependence of the Curie-Weiss constant C on T" should also cause measurements near T_0 to yield larger values of C_e than far from T_0. Such a tendency is apparently not contradicted by experiment[1,9], although a considerable scatter of C_e is observed in the experiment. The results of Sec. 5, namely that the rhombohedral phase is stable when $\mu > 0$ at low values of T and the tetragonal phase is stable at $\mu < 0$, and that in the former case the transitions can go from the tetragonal to the rhombic and to the rhombohedral phase and from the rhombic to the rhombohedral phase but not vice versa, must apparently be compared with experiment with caution. We have not taken into account quantum effects that are important at low $T \lesssim \hbar\omega_c$, as well as the presence of other "non-ferroelectric" degrees of freedom, which can lead to additional transitions. Therefore the foregoing statements must be taken apparently only as indications of a general tendency of ferroelectric transitions; in this sense, they can probably be regarded as in accord with the data in[1] on the transitions.

Let us attempt to obtain numerical estimates for $BaTiO_3$, the most investigated perovskite. The formulas in (10) have been derived for $\xi \ll 1$, but correlation effects are observed mainly where they are not small, i.e., in the vicinity of T_0. For lack of something better, we shall compare with experiment the approximation of (10) which is linear in ξ, although the "corrections" involved in this case may become comparable with the "zeroth" approximation. This nevertheless gives an idea of the order of magnitude, although such a comparison, besides the already mentioned difficulties, is aggravated also by the scatter and by the inaccuracy of the experimental data.

According to experiment[1] and formula (10), the quantities $q_{ik}(T)$ and $c_{ik}(T)$ change little in the vicinity of the transition, so that in first approximation they can be identified with the constants q_{ik} and c_{ik} in (3). According to[7,1], we have (in cgs units): $c_+ = 4.2 \times 10^{12}$, $c_- = 0.82 \times 10^{12}$, $q_+ = 2.1$, $q_- = 1.3$, $c_{44} = 1.1 \times 10^{12}$, and $q_{44} = 0.78$. Then it follows from the inequality $\nu > 0$ that $b_{11} > 3.5 \times 10^{-12}$, and from the condition $\mu > 0$ it follows that $\mu = 1 - \beta - b_{11}^{-1} \times 3.7 \times 10^{-12} > 0$. As noted, the presence of three successive transitions corresponds apparently to small μ, so that it can be assumed that $\mu \ll 1$ in $BaTiO_3$ (and $KNbO_3$).

In comparing the $\epsilon(T)$ dependence with experiment, we start from the fact that the "Curie-Weiss law" observed near T_0 is an interpolation of the relation (10) into this region:

$$\frac{T - T_{c\text{э}}}{C_{\text{э}}} \approx \frac{T - T_c}{C}(1 - \xi a_1), \quad T - T_0 \lesssim 50°. \qquad (23)$$

From the foregoing figures and from the inequality for b_{11} it follows that the quantities q^2, d^2, ϵ^2, δ^2 in (11) are all $\lesssim 0.1$–0.5, and, as will be shown below, β is also small. Therefore, in first approximation $a_1 \approx 1$, $a_2 \approx 0.35$, and $a_3 \approx 1.2$. We determine the constant C from measurements made far from the transition[9,21]: $C \approx 1.2 \times 10^5$. (Here and below, C and T are in degrees Kelvin.) We determine the constants of the left side from[22]: $C_e = 1.73 \times 10^5$, $T_0 = 393$, $T_0 - T_{ce} = 10$. Then, equating the functions and the derivatives in both sides of (23), for example at $\tau = T - T_0 = 30$, we get $T_0 - T_c \approx 24$ and for $\xi(\tau)$ we obtain $\xi(30) \approx 0.5$ and $\xi(0) \approx 0.7$. It is easy to verify that the experimentally observed 10–20% variation of C and C_e does not exert a strong influence on the value of ξ, and particularly on $\Delta\xi = \xi(\tau) - \xi(0)$. Figure 4a illustrates the temperature dependence of both halves of (23). We determined the coefficient b_{11} with the aid of[5], in which the nonlinearity coefficient B_{11} of the free crystal was measured in the interval $\tau \lesssim 30$. According to (10) this quantity is

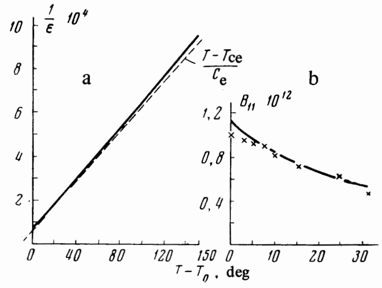

FIG. 4

equal to $b_{11}(T)\nu(T)$, where the dependence of b_{11} and ν on T denotes allowance for the correlation corrections:

$$B_{11} \approx b_{11}[\nu - \xi(a_3 - {}^1/_2 a_1 \varkappa_+ - 2a_2\varkappa_- + {}^1/_8 \varkappa_+^2 + {}^7/_{40}\varkappa_-^2)]. \quad (24)$$

Equating (24) to the experimental value of $B_{11} \approx -0.67 \times 10^{-15}$ at $\tau = 20$, we get $b_{11} \approx 4.4 \times 10^{-12}$. The corresponding values of κ_+ and κ_- are equal to 0.31 and 0.64, and the condition $\mu \lesssim 0$ yields $\beta \lesssim 0.16$. The temperature dependence of (24), together with the experimental points from[5] is shown in Fig. 4b. We note that when $\xi \sim 1$ formulas (10) apparently overestimate the correlation effects[11]. Therefore a certain overestimate of the "theoretical" curves in Fig. 4 at small τ over the experimental ones is natural, and might possibly be even larger if the "true" values of b_{11}, C, and $T_0 - T_c$ are substituted in (10). We see, however, that the chosen values describe satisfactorily the course of $\epsilon(T)$ and $B_{11}(T)$. The order of magnitude of $\xi(T)$ agrees also with formula (2). If we assume[15] that $\lambda^{1/2} \approx 0.8 \times 10^{13}$ Hz and recognize that when anisotropy is taken into account the value of s in (2) is equal not to s_t, but to some combination of s_t and s_a averaged in some manner over the angles (it is too complicated to write out here), then the results correspond to $s \approx 2 \times 10^{10}$, whereas $s_t \sim (1-1.5) \times 10^{10}$, and s_a is apparently larger by several times[15,23].

Let us discuss now the anomalies of $c_\pm$, $q_\pm$, and also of the specific heat c_V and of the coefficient of linear expansion γ_T:

$$c_v = c_{v0}\left(1 + \xi\frac{8\pi^2 T}{b_{11}C^2 c_{v0}}\right), \quad \gamma_T = \frac{d\eta}{dT} = \gamma_0\left(1 - \xi\frac{4\pi q_+}{3b_{11}Cc_+\gamma_0}\right). \quad (25)$$

Here c_{V0} and γ_0 are the specific heat and the expansion coefficient far from the transition; in $BaTiO_3$ near T_0 we have $c_{V0} \approx 15v_c^{-1}$, where v_c is the volume of the cell, and $\gamma_0 \approx 10^{-5}$ deg^{-1}. Using the foregoing estimates, we find that in $BaTiO_3$ all these anomalies are apparently small. Thus, in the interval $\tau = 30-0$ we have $\Delta\xi = \xi(30) - \xi(0) \approx -0.2$, so that in accordance with (10) we have $\Delta c_+/c_+ \sim 0.015$, $\Delta c_-/c_- \sim 0.02$, $\Delta q_+/q_+ \sim 0.1$, $\Delta q_-/q_- \sim 0.07$, $\Delta\gamma_T/\gamma_0 \sim 0.08$, and $\Delta c_V/c_{V0} \sim -0.003$ (the special smallness of Δc_V is connected with its "liberal" smallness $\sim T\epsilon_{at}^{-1}$). The observation of these anomalies called apparently for an increase in the experimental accuracy. The observed anomalies of the elastic moduli[1,7] and of the striction coefficients[24] have the correct sign, but seem to be too large to be attributed only to these effects, although, as already noted, our estimates cannot be regarded as quantitatively exact.

7. CONCLUSION

Thus, the previously advanced opinion[4] that the phenomenological theory describes well the phase transitions of the displacement types, and that the correlation effects are small in this case, is apparently incorrect. In this case, the Devonshire expansion (1) in the vicinity of and below T_0 must be regarded simply as an empirical formula, having no microscopic meaning.

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[1] F. P. Iona and G. Shirane, Ferroelectric Crystals, Pergamon, 1962.

[2] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964, Ch. XIV; Élektrodinamika sploshnykh sred [Electrodynamics of Continuous Media, Gostekhizdat, 1957, Sec. 19 (Addison-Wesley)].

[3] P. C. Kwok and P. B. Miller, Phys. Rev. 151, 387 (1966).

[4] V. G. Vaks, Zh. Eksp. Teor. Fiz. 54, 910 (1968) [Sov. Phys.-JETP 27, 486 (1968)].

[5] M. E. Drougard, R. Landauer, and D. R. Young, Phys. Rev. 98, 1010 (1955).

[6] A. K. Goswami, J. Phys. Soc. Japan 21, 1037 (1966).

[7] E. J. Huibregtse, W. H. Bessey, and M. F. Drougard, J. Appl. Phys. 30, 899 (1959).

[8] A. P. Levanyuk, Zh. Eksp. Teor. Fiz. 49, 1305 (1965) [Sov. Phys.-JETP 22, 901 (1966)].

[9] G. Rupprecht and R. O. Bell, Phys. Rev. 135, A748 (1964).

[10] W. Cochran, Adv. Phys. 9, 387 (1960); 10, 401 (1961).

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

[12] V. L. Pokrovskiĭ, Usp. Fiz. Nauk 94, 127 (1968) [Sov. Phys.-Uspekhi 11, 66 (1968)].

[13] V. L. Ginzburg, Fiz. Tverd. Tela 2, 2031 (1960) [Sov. Phys.-Solid State 2, 1824 (1960)]; Usp. Fiz. Nauk 77, 621 (1962) [Sov. Phys.-Uspekhi 5, 649 (1963)].

[14] R. A. Cowley, Phys. Rev. 134, A981 (1964).

[15] G. Shirane, B. C. Frazer, V. J. Minkiewicz, J. A. Leake, and A. Linz, Phys. Rev. Lett. 19, 234 (1967).

[16] B. Ya. Balagurov, V. G. Vaks, and B. I. Shklovskiĭ, Fiz. Tverd. Tela 12, 89 (1970) [Sov. Phys.-Solid State 12, No. 1 (1970)].

[17] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike (Quantum Field Theoretical Methods in Statistical Physics), Fizmatgiz, 1962 [Pergamon, 1965].

[18] V. G. Vaks, V. M. Galitskiĭ, and A. I. Larkin, Zh. Eksp. Teor. Fiz. 54, 1172 (1968) [Sov. Phys.-JETP 27, 627 (1968)].

[19] V. G. Vaks and A. I. Larkin, ibid. 49, 975 (1965) [22, 678 (1966)].

[20] A. I. Larkin and S. A. Pikin, ibid. 56, 1664 (1969) [29, 891 (1969)].

[21] Yu. M. Poplavko, V. G. Tsykalov, Izv. AN SSSR ser. fiz. 33, 1119 (1969). V. N. Murzin and A. I. Demeshina, Fiz. Tverd. Tela 6, 182 (1964) [Sov. Phys.-Solid State 6, 144 (1964)]. J. Ballantyne, Phys. Rev. 136, 429 (1964).

[22] M. E. Drougard and D. R. Young, Phys. Rev. 95, 1152 (1954).

[23] Y. Yamada, G. Shirane, and A. Linz, Phys. Rev. 177, 848 (1969).

[24] G. Schmidt, Z. Physik 145, 534 (1956).

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