COMPLEX PHASE TRANSITIONS IN CRYSTALS

D. E. KHMEL'NITSKIĬ

L. D. Landau Institute of Theoretical Physics, U.S.S.R. Academy of Sciences

Submitted May 26, 1971

Zh. Eksp. Teor. Fiz. 61, 2110–2122 (November, 1971)

Complex second-order phase transitions in crystals are studied, i.e., those transitions which are accompanied by lattice distortions associated not only with the transition parameter but also with other noncritical parameters (the polarization, shear deformation, etc.).[1,2] The consequences of the scaling hypothesis are examined for these transitions. It is shown that, apart from the two usual critical indices, for these substances there exist additional indices corresponding to polarizabilities of the noncritical degrees of freedom. Relations are found between the indices of the noncritical quantities. The effect of long-range forces is discussed. It is shown that the asymmetric phase arises in complex ferroelectrics at $T < T_c$ in a single-domain state. The question of dielectric losses in com plex ferroelectrics is discussed. For transitions of the order-disorder type, this phenomenon is analogous to the anomalous absorption of sound and the results are analogous to those of Landau and Khalatnikov, and Levanyuk. For displacive-type transitions, there exists in the loss spectrum a threshold singularity at a frequency equal to twice the frequency of the critical branch. Observation of this singularity can resolve the question of the type of transition.

1. INTRODUCTION

THE behavior of most known ferroelectrics in the region of the phase transition is well described by the Ginzburg–Devonshire theory, which assumes that the polarization **P** is the order parameter. However, in a number of substances, one observes a relatively slow increase in polarization in the asymmetric phase, a singularity in the susceptibility that is weak compared with that given by the Curie–Weiss law, and sometimes even a change in the number of atoms in the unit cell during the phase transition.

Such a possibility was predicted by Indenbom,[1] who considered the case when not the polarization but some other lattice deformation η serves as the order parameter; in the expansion of the free energy in powers of η, the term $\eta^2 P$ is allowed by symmetry, and, thanks to this term, spontaneous polarization arises in the asymmetric phase. The dielectric properties of crystals in the region of a complex phase transition of this type were studied by Levanyuk and Sannikov[2] in the framework of a phenomenological theory. In the present paper, we examine the critical behavior of different quantities close to the complex phase transition point and establish relations between the possible critical indices. Such a treatment may turn out to be useful not only for complex ferroelectric transitions, but also in general for all transitions characterized by a many-component order parameter. For example, in the case of cubic ferroelectrics (of the $BaTiO_3$ type), one can find a connection between the indices of the anomalous part of the shear modulus and of the spontaneous shear deformation.

Most complex ferroelectrics are uniaxial. Dipole–dipole forces are important in this case and their role is discussed in Sec. 4. In Secs. 5 and 6, we consider the question of the dielectric losses in the region of the transition point of a complex phase transition of the order–disorder and displacive types, and the question of the possibility of identifying transitions of the displacive type. The properties of the critical indices are discussed in the Appendix using the four-dimensional model as an example.

2. SYMMETRY PROPERTIES

We shall assume that the phase transition is characterized by the order parameter η_i (i = 1, 2 or i = 1, 2, 3), which transforms according to the irreducible representation τ of dimensionality f. The Green function $G_{ij}(\mathbf{r}) = \langle \eta_i(0)\eta_j(\mathbf{r})\rangle$ transforms according to the representation $[\tau^2]$:

$$\hat{T}_g G_{ij}(\mathbf{r}) = [\tau^2(g)]_{ij}^{lm} G_{lm}(\hat{g}\mathbf{r})$$

and $[\tau^2]$ can be decomposed into the irreducible representations $\tau^{(\lambda)}$. This means that

$$G_{ij}(\mathbf{r}) = \sum_\lambda G_{ij}^{(\lambda)}(\mathbf{r})$$

where $G_{ij}^{(\lambda)}$ transforms like $\varphi_{ij}^{(\lambda)}$ under the action of $\hat{T}_g$, according to the irreducible representation $\tau^{(\lambda)}$:

$$\varphi_{ij}^{(\lambda)} = \tau_{ij}^{(\lambda)lm} \varphi_{lm}^{(\lambda)}.$$

For the φ_{ij}, we have the normalization rule

$$\varphi_{ij}^{(\lambda)} \varphi_{ij}^{(\lambda')} = f_\lambda \delta_{\lambda\lambda'}$$

where f_λ is the dimensionality of the representation $\tau^{(\lambda)}$; $\varphi_{ij}^{(0)} = f^{-1/2}\delta_{ij}$.

Among the $\lambda^{(\lambda)}$ into which $[\tau^2]$ was decomposed, there is only one identical representation $\tau^{(0)}$ and no τ (Landau's rule). These dimensionalities satisfy the condition $\sum_\lambda f_\lambda = f^2$.

Below we shall use the notation

$$G^{(\lambda)}(\mathbf{r}) = \varphi_{ij}^{(\lambda)} G_{ij}^{(\lambda)}(\mathbf{r}), \qquad G_{ij}^{(\lambda)}(\mathbf{r}) = f_\lambda^{-1} \varphi_{ij}^{(\lambda)} G^{(\lambda)}(\mathbf{r}).$$

If among the $\tau^{(\lambda)}$ there are some that are contained also in the general representation of the group, this means that the crystal symmetry permits the existence in the free energy of a term of the form

$$\xi_\lambda \varphi_{ij}^{(\lambda)} \eta_i \eta_j, \tag{1}$$

where ξ_λ is some parameter characterizing the state of the crystal and corresponding to the irreducible representation $\tau^{(\lambda)}$. One of these parameters is the hydrostatic stress deformation div **u** corresponding to the strictional term η_i^2 div **u**. There are no other parameters corresponding to the identical representation $\tau^{(0)}$. But fairly many examples of terms of the form (1) with $\lambda \neq 0$ can be found. There are, for example, the shear part of the striction in ferromagnets

$$(u_{\alpha\beta} - {}^1/_3\delta_{\alpha\beta}u_{\gamma\gamma})(M_\alpha M_\beta - {}^1/_3\delta_{\alpha\beta}M^2)$$

the term connected with the magneto-electric effect in antiferromagnets $\mathbf{P}[\mathbf{M}_1 \times \mathbf{M}_2]$, and the Indenbom term $P_z\eta_1\eta_2$ in the free energy close to a complex ferroelectric transition. Among the quantities ξ, we cannot have components of the magnetic moment, since on time reversal, $\mathbf{M} \to -\mathbf{M}$. (The case of a transition between different magnetically ordered structures is an exception and is not considered here.)

In the region of applicability of the phenomenological theory, the Landau expansion for the free energy has the form

$$F - F_0 = \frac{1}{2}a\eta_i^2 + \frac{1}{2}\sum_\lambda s^{(\lambda)}(\nabla\nabla')^{(\lambda)}\varphi_{ij}^{(\lambda)}\eta_i(\mathbf{r})\eta_j(\mathbf{r}')\,|_{r'\to r}$$
$$+ \frac{1}{4}\sum_\alpha b_\alpha(\eta^4)_\alpha + \sum_\lambda\left\{d_\lambda\xi_\lambda\varphi_{ij}^{(\lambda)}\eta_i\eta_j + h_\lambda\xi_\lambda + \frac{1}{2\chi_0^{(\lambda)}}\xi_\lambda^2\right\} + \ldots. \tag{2}$$

Here $(\eta^4)_\alpha$ are the possible fourth-order invariants constructed from the components of η; $(\eta^4)_0 = (\eta_i^2)^2$. The term with $(\nabla\nabla')^{(\lambda)}$ is constructed as follows: ∇ transforms according to the vector representation V (reducible, generally speaking), and in the decomposition of V into irreducible representations there may also be some of the $\tau^{(\lambda)}$ (V always contains $\tau^{(0)}$); the quantity $(\nabla\nabla')^{(\lambda)}\varphi_{ij}^{(\lambda)}$ is a bilinear combination, transforming as $\varphi_{ij}^{(\lambda)}$, of components of the gradient. The quantity h_λ is the field interacting with ξ_λ. This field may be the pressure p, the shear part $\sigma_{\alpha\beta} + {}^1/_3 p\delta_{\alpha\beta}$ of the elastic stress tensor, or components of the electric field **E**. The term $(\chi_0^{(\lambda)})^{-1}$ corresponds to the inverse susceptibility far from the transition point. It is not specially large as $T \to T_c$. The quantities $s^{(\lambda)}$, which also do not have singularities at the transition point, are related to the magnitudes of the corresponding interactions. For example, in ferromagnets, where the principal interaction (exchange) possesses spherical symmetry, the largest term will be $s^{(0)}(\nabla\nabla')(\mathbf{M}(\mathbf{r})\cdot\mathbf{M}(\mathbf{r}'))_{\mathbf{r}'\to\mathbf{r}}$, and the remaining gradient terms are small to the extent that the anisotropic interactions are small. There are no linear terms in the gradients by virtue of Lifshits' rule.

In the region of applicability of expansion (2), the Green function at small k is equal to

$$G_{ij}^{-1}(k) = a\delta_{ij} + \sum_\lambda s^{(\lambda)}\varphi_{ij}^{(\lambda)}(k^2)^{(\lambda)}. \tag{3}$$

In this Section we shall assume that there are no long-range forces that do not fall off with distance, and therefore, when $\mathbf{k} \to 0$, $G(\mathbf{k}) \to G(0)$. In precisely the same way, $G(\mathbf{r})_{\mathbf{r}\to 0} = G(0)$ at small distances and does not depend on the directions of $\mathbf{r}/r$ or $\mathbf{k}/k$.

We shall perform a coordinate transformation $\mathbf{r} \to \mathbf{r}'$, $\mathbf{r} = \hat{g}\mathbf{r}'$. Then $G_{ij}^{(\lambda)}(\mathbf{r}) = \tau^{(\lambda)}(g)_{ij}^{lm}G_{lm}^{(\lambda)}(\hat{g}\mathbf{r})$ and, going over to $G^{(\lambda)}(\mathbf{r})$, we obtain

$$G^{(\lambda)}(\mathbf{r}) = \chi_\lambda(g) f_\lambda^{-1} G^{(\lambda)}(\hat{g}\mathbf{r}) \tag{4}$$

where $\chi_\lambda(g)$ is the character of the matrix $\tau^{(\lambda)}(g)$. For $\mathbf{r} = \mathbf{r}' \equiv 0$, it follows from equality (4) that either all the matrices $\tau^{(\lambda)}(g)$ are the identical ones ($\lambda = 0$), or $G^{(\lambda)}(\mathbf{r} = 0) = 0$. It can be proved analogously that $G^{(\lambda)}(\mathbf{k} = 0) = 0$ when $\lambda \neq 0$.

The inverse matrix $[G^{-1}]_{ij}$, like G_{ij}, can be expanded in the irreducible tensors $\varphi_{ij}^{(\lambda)}$;

$$[G^{-1}]_{ij} = \sum_\lambda G^{-1(\lambda)}\varphi_{ij}^{(\lambda)}, \tag{5}$$

$$\varphi_{ij}^{(\lambda)}\varphi_{jl}^{(\lambda')} = \frac{f_\lambda}{f}\delta_{il}\delta_{\lambda\lambda'} + \psi_{il}^{\lambda\lambda'} \tag{6}$$

where ψ_{ij} are symmetric matrices with zero trace $\psi_{ii} = 0$, $\psi_{ij}^{00} = 0$, $\psi_{ij}^{\lambda 0} = f^{-1/2}\varphi_{ij}^{(\lambda)}$ when $\lambda \neq 0$. Multiplying by G_{jl} and using (6), we obtain

$$\sum_\lambda f_\lambda G^{(\lambda)}G^{-1(\lambda)} = f, \tag{7}$$

$$\sum_{\lambda\lambda'}\psi_{ij}^{\lambda\lambda'}G^{(\lambda)}G^{-1(\lambda')} = 0. \tag{8}$$

If we separate out the terms with $\lambda = 0$, then

$$G^{(0)}G^{-1(0)} + {\sum_\lambda}' f_\lambda G^{(\lambda)}G^{-1(\lambda)} = f, \tag{7a}$$

$${\sum_\lambda}'\varphi_{ij}^{(\lambda)}[G^{(\lambda)}G^{-1(0)} + G^{(0)}G^{-1(\lambda)}] + {\sum_{\lambda\lambda'}}'\psi_{ij}^{\lambda\lambda'}G^{-1(\lambda)}G^{(\lambda')} = 0. \tag{8a}$$

For $k \to 0$, when $G^{(\lambda)} \to 0$ for $\lambda \neq 0$, and $G^{(0)} \neq 0$, it follows from (7a) and (8a) that

$$G^{-1(0)}(k) = \frac{f}{G^{(0)}(k)}, \qquad G^{-1(\lambda)}(k) = \frac{fG^{(\lambda)}(k)}{G^{(0)2}(k)}. \tag{9}$$

The equality (9) is fulfilled for all k at which $G^{(\lambda)}(k) \ll G^{(0)}(k)$.

3. THE SCALING HYPOTHESIS. RELATION BETWEEN THE INDICES

The scaling hypothesis for critical fluctuations in the vicinity of transition points[3-5] consists in the assumption of scale invariance at $T = T_c$, i.e., that all the exact relations remain valid after the transformations $\mathbf{r} \to a\mathbf{r}$, $\eta \to z^{1/2}(a)\eta$. It is assumed that z(a) has a power dependence $z \sim a^\nu$. For $T \neq T_c$, there is a length $m^{-1}(\tau)$, called the correlation length ($\tau = |T - T_c|/T_c$). For $k \gg m$, all the dependences obtained for $T = T_c$ remain valid. In the region of yet greater k, all the results must be "matched" with the results of the phenomenological theory.

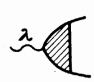
We shall assume that in our many-component case there is scale invariance at $T = T_c$, while at $T \neq T_c$ there is one scalar correlation length $m^{-1}(\tau)$. Then at $T = T_c$, we shall have $G^{(\lambda)}(k) \sim k^{\nu-3}$ for all λ. We saw in deriving the equality (9) that the symmetry properties permit the inequality $G^{(\lambda)} \ll G^{(0)}$ for all k. This, however, is forbidden by the scale invariance: on transforming $r \to ar$, all the $\eta_i \to z^{1/2}(a)\eta_i$, and $G^{(\lambda)} \to z(a)G^{(\lambda)}$, irrespective of λ. In addition, at large k there must be "matching" with the phenomenological expression (3), in which the different λ enter equally.

In the region $k \ll m(\tau)$, only $G^{(0)}(k) \sim G^{(0)}(m) \sim m^{\nu-3}$ remains finite. All the other $G^{(\lambda)}(k) \to 0$ as $k \to 0$. In order to estimate $G^{(\lambda)}(k)$ as $k \to 0$, we need to construct from the components of **k** a quantity transforming according to $\tau^{(\lambda)}$. If there exists such a quantity, e.g., quadratic in k, then

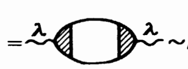
$$G^{(\lambda)}(k) \sim \frac{(k^2)^{(\lambda)}}{m^2} G^{(\lambda)}(m) \sim (k^2)^{(\lambda)} m^{\nu-5}, \qquad k \ll m, \quad \lambda \neq 0. \qquad (10)$$

For the amplitudes $\Gamma_n(k)$ when $k \gg m$, there exists the usual estimate $\Gamma_n \sim k \exp\{c - n\nu/2\}$ (cf., e.g., [4]). For $k \ll m$, the quantities $\Gamma_n^{(\alpha)}$ to which correspond the invariants $(\eta^n)_\alpha$ remain finite: $\Gamma_n^{(\alpha)}(k) \sim \Gamma_n^{(\alpha)} \sim m^{3-n\nu/2}$, while the others go to zero like $G^{(\lambda)}(k)$ as $k \to 0$ when $\lambda \neq 0$.

Responses to an external stimulus $\xi_\lambda \varphi_{ij}^{(\lambda)}$ are described by three-point amplitudes $\mathcal{T}_\lambda(k)$. Each of these has its own index:

$\mathcal{T}_\lambda(k) =$  $\sim k^{\delta_\lambda}$ (11)

The corresponding susceptibility is made up of the zeroth term $\chi_0^{(\lambda)-1}$ and the anomalous part $d_\lambda^2 \Pi_\lambda(m)$, where $\Pi_\lambda(k)$ is the polarization operator,

$\pi_\lambda(k) =$  $\sim k^{2(\delta_\lambda+\nu)-3}$ (12)

The quantity $\Pi_0(m)$ determines the anomalous parts of the specific heat and of the hydrostatic stress modulus. Since ξ_0 is a scalar having the same symmetry as $\tau = |T - T_c|/T_c$, we have

$$\mathcal{T}_c(k) = \partial G^{-1(0)}(k) / \partial\tau$$

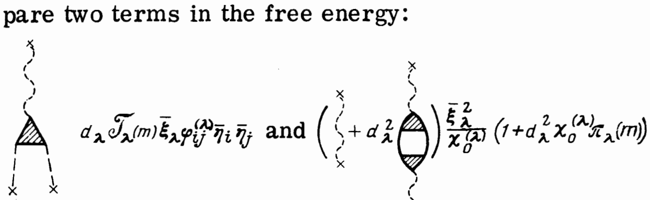
$\xi_0 \sim \tau$ and δ_0 is not an independent index, but can be expressed in terms of the temperature index β,

$$m = \tau^\beta, \quad m^{\delta_0} \sim \tau^{\beta\delta_0} \sim m^{3-\nu}/\tau \sim \tau^{\beta(3-\nu)-1}, \qquad (13)$$

$$\delta_0 = 3 - \nu - 1/\beta. \qquad (14)$$

The polarizabilities $\Pi_\lambda(m)$ with $\lambda \neq 0$ describe the anomalous parts of the shear modulus in cubic ferroelectrics and ferromagnets or of the dielectric susceptibility in complex ferroelectrics.

In order to find the temperature dependence of the deformation $\bar{\xi}_\lambda$ when $T < T_c$, it is necessary to compare two terms in the free energy:



Hence

$$\bar{\xi}_\lambda \sim \frac{d_\lambda \chi_0^{(\lambda)} \mathcal{T}_\lambda(m) \varphi_{ij}^{(\lambda)} \bar{\eta}_i \bar{\eta}_j}{1 + d_\lambda^2 \chi_0^{(\lambda)} \Pi_\lambda(m)}. \qquad (15)$$

Taking into account (11)–(13) and also the fact that $\bar{\eta} \sim m^{\nu/2}$, we obtain the dependence $\bar{\xi}_\lambda(\tau)$. In doing this, it is necessary to recognize that for small $d_\lambda^2 \chi_0^{(\lambda)}$ the quantity $d_\lambda^2 \chi_0^{(\lambda)} \Pi_\lambda$ can be small in the critical region also. Therefore,

$$\bar{\xi}_\lambda(\tau) \sim d_\lambda \chi_0^{(\lambda)} \begin{cases} \tau^{\beta(\nu+\delta_\lambda)}, & d_\lambda^2 \chi_0^{(\lambda)} \Pi_\lambda(m) < 1, \\ \dfrac{1}{d_\lambda^2 \chi_0^{(\lambda)}} \tau^{\beta[3-(\nu+\delta_\lambda)]}, & d_\lambda^2 \chi_0^{(\lambda)} \Pi_\lambda(m) > 1. \end{cases} \qquad (16)$$

In an external field h_λ, a displacement ξ_λ arises, and for $T > T_c$,

$$\bar{\xi}_\lambda(h) \sim \frac{\chi_0^{(\lambda)} h_\lambda}{1 + d_\lambda^2 \chi_0^{(\lambda)} \Pi_\lambda(m)} \qquad (17)$$

which gives a correction to $G^{-1(\lambda)}$: $\Sigma_h^{(\lambda)} \sim \bar{\xi}_\lambda(h)$. Now $G^{-1(\lambda)}(k) \neq 0$ when $k \to 0$ also. Therefore, when $G^{-1(0)}(0) \to 0$ as $T \to T_c$, $G^{-1(\lambda)}$ begins to make an important contribution to $G^{(0)}$. As a result, the singularity in $G^{(0)}$ is shifted, corresponding to a shift in T_c. Terms of the type (17) become important when

$$G^{(0)}(m) G^{-1(\lambda)}(h, m) \sim 1.$$

Therefore, $\Delta\tau$ is determined from the relation

$$\bar{\xi}_\lambda(h) \sim [m(\Delta\tau)]^{3-\nu}. \qquad (18)$$

It was assumed everywhere above that all the $\tau^{(\lambda)}$ are different. If there are equivalent $\tau^{(\lambda)}$ and $\tau^{(\lambda')}$ among them, then $\delta_\lambda = \delta_{\lambda'}$.

The power-law character of the scaling laws is associated to a considerable extent with the three-dimensionality of momentum space. If this were four-dimensional, the contribution of fluctuations to the thermodynamic functions would grow only logarithmically as $k \to 0$ and $T \to T_c$, the problem could be solved,[6] and the results would differ from the predictions of the phenomenological theory only by powers of logarithms. The powers of the logarithms depend on the symmetry of the Hamiltonian and play the role of the critical indices. Therefore, the study of four-dimensional models can provide important additional lines of reasoning concerning the critical indices in real systems. The results of the solution of one four-dimensional model of a phase transition with a multidimensional order parameter are discussed in the Appendix.

4. EFFECT OF LONG-RANGE FORCES

Up to now we have not taken into account the long-range (dipole-dipole and elastic) forces. Allowance for these, however, can change the results markedly. An example is the result of Larkin and Pikin,[7] who showed that when the interaction with the acoustic phonons is taken into account in the elastically isotropic model, a second-order transition is transformed into a first-order transition.

Following [7] and [8], we write the free energy for a complex ferroelectric in the form of a functional integral:

$$\mathcal{F} - \mathcal{F}_0 = -T \ln \int dP_i\, d\eta_{1i}\, d\eta_{2i} \exp\Big\{-\frac{1}{T}\sum_i \Big[\mathcal{H}_i(\eta_1, \eta_2) - \mathbf{P}_i\mathbf{E}_i + cP_i\eta_{1i}\eta_{2i} + \frac{1}{2\chi_0}P_i^2 + \frac{E_i^2}{8\pi v_0}\Big]\Big\}, \qquad (19)$$

where

$$\mathcal{H}_i(\eta_1, \eta_2) = \frac{1}{2}a(\eta_{1i}^2 + \eta_{2i}^2) + \frac{b_1}{4}(\eta_{1i}^2 + \eta_{2i}^2)^2 + \frac{b_2}{2}(\eta_{1i}\eta_{2i})^2 + \sum_{j\neq i} V_{ij}(\eta_{1,2i} - \eta_{1,2j})^2,$$

and it is assumed that $\mathbf{P}$ is directed along the z-axis.

If there were no long-range forces, i.e., the term $P_i \cdot E_i$ were absent, by taking the integral over the P_i we would reduce the phase-transition problem to another such problem, with the replacement $b_2 \to b_2 - c^2\chi_0$, and the correlator of the P_i would be equal to

$$\langle P_i P_j\rangle = \frac{1}{\chi_0}(1 + c^2\chi_0 \langle \eta_{1i}\eta_{2i}\eta_{1j}\eta_{2j}\rangle) = \frac{1 + c^2\chi_0 \Pi_{12}(r_{ij})}{\chi_0}. \quad (20)$$

If $\Pi_{12}(k \to 0) \to \infty$, then $\chi^{-1} \sim \langle P_i P_j\rangle_{k\to 0} \to 0$.

If we take the long-range forces into account, then it is necessary to represent

$$P_i = P + \frac{1}{N}\sum_{k\neq 0} e^{ikr_i}P_k, \qquad \mathbf{E}_i = \mathbf{E} + \frac{1}{N}\sum_{k\neq 0} e^{ikr_i}\mathbf{E}_k$$

and to express $\mathbf{E}_k$ in terms of $\mathbf{P}_k$ from Maxwell's equations: $\mathbf{E}_k = 4\pi \mathbf{k} k_z P_k / k^2$. We shall consider the transition when $E = 0$. Integrating over the P_i, we obtain in the exponent of the statistical exponential

$$-\frac{1}{T}\left\{\sum_i \mathscr{H}_i(\eta_1, \eta_2) - \frac{c^2\chi_0}{N}\sum_{ij}\sum_{k\neq 0}\eta_{1i}\eta_{2i}\eta_{1j}\eta_{2j}\frac{e^{ikr_i}}{1 + 4\pi k^2 k^{-2}\chi_0}\right\}. \quad (21)$$

Thus, allowance for the dipole-dipole forces leads to an additional interaction. This interaction $(\eta_1\eta_2)_i$ and $(\eta_1\eta_2)_j$ does not fall off with distance and depends on the angle between the ferroelectric axis z and the direction of $\mathbf{r}_{ij}$. It may be hoped that the contribution of this interaction to the thermodynamic functions is not so long as $c^2\chi_0\Pi_{12}(\tau) < 1$, but on closer approach to T_c it can begin to play an important role. In particular, the fact that many known complex ferroelectrics undergo a first-order transition close to a second one may be explained, possibly, by the effect of this interaction.

The long-range pair interactions of $(\eta^2)_i$ and $(\eta^2)_j$, which depend on the angles of $\mathbf{r}_{ij}$, arise fairly often when long-range forces are taken into account. For example, in cubic ferromagnets there is an additional interaction, associated with the strictional interaction via the acoustic phonons.

Another manifestation of the dipole-dipole interaction is the division of the sample into domains. In the region of a complex ferroelectric transition, this phenomenon has a characteristic singularity. The point is that the wall tension energy is entirely determined by the distribution of $\eta_1(y)$ and $\eta_2(y)$. The characteristic wall thickness in the region of applicability of the phenomenological theory is $\Delta \sim (T_c - T)^{-1/2}$, and the specific free energy loss within the wall is of order $(T_c - T)^2$. Therefore, the wall tension is $\sigma \sim (T_c - T)^{3/2}$. If the domain dimensions are equal to a, while the dimension of the sample in the direction of the z-axis is equal to l, then the surface-tension energy is proportional to σl, while the energy associated with the emergence of a domain to the surface is P^2a^2. In complex ferroelectrics, $P \sim T_c - T$. Therefore, the domain dimension a corresponding to the minimum energy is proportional to

$$a \sim (\sigma l / P^2)^{1/2} \sim (T_c - T)^{-1/4} \quad (22)$$

and tends to infinity as $T \to T_c$. The increase in domain size as $T \to T_c$ is a manifestation of the weakness of the dielectric anomalies in a complex ferroelectric transition. As Levanyuk and Sannikov [2] have already remarked, the asymmetric phase at $T < T_c$ arises at once in a single-domain state.

5. DIELECTRIC LOSSES IN COMPLEX FERROELECTRICS. ORDER–DISORDER TRANSITION

In this and the following sections, we shall consider the question of dielectric loss anomalies in the region of a complex ferroelectric transition. The treatment, unlike the preceding one, will be carried out in the framework of self-consistent field theory, and fluctuational corrections will be taken into account only when $T > T_c$ in ferroelectrics of the order-disorder type, when this theory does not give an anomalous contribution. Self-consistent field theory is applicable in a relatively broad range of temperatures for transitions of the displacive type. For order-disorder transitions, the region of applicability of such a theory is narrower, but all the qualitative results obtained in this section are also applicable in the region of strong critical fluctuations.

Following Levanyuk and Sannikov, [2] we write the free energy in the form

$$F - F_0 = \frac{1}{2}a(\tau)(\eta_1^2 + \eta_2^2) + \frac{b_1}{4}(\eta_1^2 + \eta_2^2)^2 + \frac{b_2}{2}\eta_1^2\eta_2^2 + cP\eta_1\eta_2 + \frac{1}{2\chi_0}P^2. \quad (23)$$

In this section we shall be interested only in the case of an order-disorder transition and in the region of small frequencies, where the motion of η_1 and η_2 has a purely relaxational character. Therefore, it is sufficient to confine ourselves to a dissipative function of the form $Q = -\gamma(\dot\eta_1^2 + \dot\eta_2^2)$. The quantity γ has the sense of a coefficient of friction and has no singularities as $T - T_c$. When $T < T_c$, two states are possible. If $\Delta = b_2 - c^2\chi_0 > 0$, then $\eta_1^0 = (-a/\beta)^{1/2}$, $\beta = b_1 - \Delta/2$, $\eta_2^0 = 0$, and $P^0 = 0$. But if $\Delta < 0$, then $\eta_1^0 = \pm\eta_2^0 = (-a/2\beta)^{1/2}$, and $P^0 = -c\chi_0\eta_1^0\eta_2^0 = \mp c\chi_0 a/2\beta$. In both cases, the deviation of P from the equilibrium value P^0 induces a deviation of η_1 and η_2 from η_1^0 and η_2^0, which, thanks to the relaxational character of the motion of η_1 and η_2, leads to losses similar to the relaxational attenuation of sound found by Landau and Khalatnikov. [9]

We shall consider, for example, the ferroelectric case $\Delta < 0$, $\eta_{1,2} = \eta^0 + \eta'_{1,2}$, $P = P^0 + P'$. The equations of motion for $\eta'_{1,2}$ and P' are obtained by the known method after differentiation of F and Q. By adding the equation for η'_2 to the equation for η'_1, we obtain

$$(a - i\gamma\omega + 6\beta\eta_0^2 + c^2\chi_0\eta_0^2)(\eta_1' + \eta_2') = -2c\eta_0 P' \quad (24)$$

$$\chi_0^{-1}P' + c\eta_0(\eta_1' + \eta_2') = 0. \quad (25)$$

Expressing $\eta'_1 + \eta'_2$ from (24) in terms of P' and substituting into (25), we obtain

$$\chi^{-1} = \chi_0^{-1}\left(1 - \frac{2c^2\chi_0\eta_0^2}{-2a + c^2\chi_0\eta_0^2 - i\gamma\omega}\right). \quad (26)$$

Putting $\omega \to 0$, we find

$$\frac{2c^2\chi_0\eta_0^2}{2a + c^2\chi_0\eta_0^2} = \frac{2c^2\chi_0}{4\beta - c^2\chi_0} = \chi_0\Delta(\chi^{-1})$$

where $\Delta(\chi^{-1})$ is the discontinuity in the inverse susceptibility in the phenomenological theory. Assuming that $\chi_0\Delta(\chi^{-1}) \ll 1$, we obtain for the tangent of the loss angle a formula analogous to the Landau–Khalatnikov formula[9] for the attenuation of sound,

$$\operatorname{tg}\delta = \frac{\operatorname{Im}\chi}{\chi} = \Delta(\chi^{-1})\frac{\omega\gamma^*}{1+(\omega\gamma^*)^2}. \qquad (27)$$

Here $\gamma^* = \gamma/2a(4\beta - c^2\chi_0) \sim (T_c - T)^{-1}$ is the effective inverse relaxation time, which increases as $T \to T_c$.

An analogous calculation can be performed for the nonferroelectric case $\Delta > 0$. As a result, a formula of the relaxational type (27) is valid for $T < T_c$. The presence of critical relaxational losses during a nonferroelectric transition may thus serve as an indication of the presence in the free energy of terms of the form $\eta^2 P$.

When $T > T_c$, there is no order parameter and the relaxational contribution to the losses is therefore equal to zero. In the vicinity of the transition point the fluctuations of η increase sharply. Scattering of the polarization vibrations by these inhomogeneous fluctuations leads to losses analogous to the sound absorption for $T > T_c$ calculated by Levanyuk.[10]

The equation of motion for η_μ has the form

$$a\eta_\mu - s\nabla^2\eta_\mu + \gamma\dot{\eta}_\mu + {}^1/_2 c\sigma_{\mu\nu}\eta_\nu P = f_\mu. \qquad (28)$$

Here $f_\mu(\mathbf{r}, t)$ is the fluctuational force, $\langle f_\mu \rangle = 0$, and $\langle f_\mu(\mathbf{r}, t) f_\nu(\mathbf{r}', t')\rangle = \gamma T\delta_{\mu\nu}\,\delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$. We now separate from η_μ the terms corresponding to the equilibrium fluctuations of η_μ^0 and the term associated with the change of $P\eta'_\mu$ ($\eta'_\mu \ll \eta_\mu^0$, $\eta' \sim P$). Therefore,

$$\langle \eta_\mu(\mathbf{k}, \omega)\eta_\nu(\mathbf{k}'\omega')\rangle = \frac{\gamma T}{(2\pi)^4}\delta_{\mu\nu}\delta(\omega + \omega')\delta(\mathbf{k} + \mathbf{k}') \times [(a + sk^2)^2 + \gamma^2\omega^2]^{-1},$$

$$\eta_\mu' = -\frac{1}{2}c\sigma_{\mu\nu}\int_{-\infty}^{t} dt' \int d\mathbf{r}' g(t - t', \mathbf{r} - \mathbf{r}')\eta_\nu^0(\mathbf{r}', t')P(t') \qquad (29)$$

where $g(\mathbf{r}, t)$ is the Green's function of the linear part of Eq. (28). Substituting η'_μ into the equation for P

$$\chi_0^{-1}P + \frac{c}{2}\sigma_{\mu\nu}\eta_\mu\eta_\nu = 0$$

we obtain

$$\chi^{-1}(\omega) = \chi_0^{-1}\left(1 - \frac{1}{2}\chi_0 c^2 K(\omega)\right),$$

$$K(\omega) = K_1 + iK_2 = \int_0^\infty dt' \int d\mathbf{R}\, e^{i\omega t'} g(t, \mathbf{R})\langle \eta_\mu^0(\mathbf{r}, t)\eta_\mu^0(\mathbf{r} - \mathbf{R}, t - t')\rangle. \qquad (30)$$

Using the expression $g(\omega, k) = (2\pi)^{-4}[a + sk^2 + i\gamma\omega]^{-1}$, we obtain finally

$$K_1(y) = \frac{T}{4\pi\sqrt{s^3 a}}I_1(y), \quad K_2(y) = \frac{Ty}{4\pi\sqrt{s^3 a}}I_2(y) \qquad (31)$$

where $y = \gamma\omega/2a$,

$$I_1(y) = \int_{-\infty}^{+\infty}\frac{x^2\,dx}{(1 + x^2)^2 + y^2} = \frac{\pi}{y\sqrt{2}}[(1 + y^2)^{1/2} - 1]^{1/2}, \qquad (32)$$

$$I_2(y) = \int_{-\infty}^{+\infty}\frac{x^2\,dx}{(1 + x^2)[(1 + x^2)^2 + y^2]} = \frac{\pi}{y^2}\left\{\frac{1}{\sqrt{2}}[1 + (1 + y^2)^{1/2}]^{1/2} - 1\right\}. \qquad (33)$$

For $y \gg 1$, we have $K_1 \approx K_2 \approx T/4\sqrt{s^3\gamma\omega}$.

For small frequencies, $y \to 0$, and the fluctuational correction to the real part has the usual form:

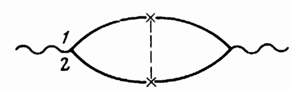
$$K_1 \approx T/8s^{3/2}a^{1/2} \sim (T - T_c)^{-1/2}.$$

6. COMPLEX FERROELECTRICS OF THE DISPLACIVE TYPE

A theory of the transitions in such crystals may be constructed analogously to the theory[11] of transitions in perovskites. As a result, the constants of the phenomenological theory are expressed in terms of microscopic quantities, and the fluctuational corrections turn out to be small to the extent that the anharmonic interaction is small. Therefore, the smallness of the anomalous part of the susceptibility can serve as an indication of a displacive-type transition. Measurements of high-frequency dielectric losses can give another method for identifying transitions of the displacive type.

To calculate the losses, we shall follow the work of Balagurov, Vaks, and Shklovskiĭ.[12] Exactly as in [12],

$$\operatorname{tg}\delta = \frac{\operatorname{Im}\Sigma(\omega)}{\Omega^2 - \omega^2} = \frac{2\omega\Gamma(\omega)}{\Omega^2 - \omega^2}, \qquad (34)$$

$\operatorname{Im}\Sigma(\omega) =$ 

$$= 2\omega\frac{\pi T}{16}\sum_{\mathbf{k}}|V_{012}^{(3)}(0, \mathbf{k}, -\mathbf{k})|^2 \times \frac{\{\delta[\omega - \omega_1(\mathbf{k}) - \omega_2(\mathbf{k})] + 2\delta[\omega + \omega_1(\mathbf{k}) - \omega_2(\mathbf{k})]\}}{\omega_1^2(\mathbf{k})\omega_2^2(\mathbf{k})}. \qquad (35)$$

Here Ω is the frequency of the "rigid" polarizational optical branch, $V_{012}^{(3)}$ is the anharmonic interaction potential of this branch with the doubly degenerate critical branch; $V_{012}^{(3)}$ is proportional to the quantity c from formula (23); $\omega_1(\mathbf{k})$ and $\omega_2(\mathbf{k})$ are the frequencies of the critical vibrations; $\omega_1(0, T) = \omega_2(0, T) = \omega_c(T) \sim |T - T_c|^{+1/2}$.

For $\mathbf{k} \neq 0$, the degeneracy is lifted and $\omega_1(\mathbf{k}) \neq \omega_2(\mathbf{k})$. For concreteness, we shall consider the case of D_{2d} symmetry in the paraphase, corresponding, for example, to $Gd_2(MoO_4)_3$.[13] In this group there is only one two-dimensional representation, E(x, y).[14] By a standard method, one can see that for $\mathbf{k} \to 0$,

$$G_{ij}^{-1}(\mathbf{k}, \omega_n) = \delta_{ij}[\omega_c^2 + \omega_n^2 + sk_\perp^2 + s_z k_z^2] + s_2 k_x k_y(\delta_{ix}\delta_{jy} + \delta_{iy}\delta_{jx}) + s_1(k_x^2 - k_y^2)(\delta_{ix}\delta_{jx} - \delta_{iy}\delta_{jy}) \qquad (36)$$

whence the eigenfrequencies $\omega_{1,2}(\mathbf{k})$ are equal to

$$\omega_{1,2}^2(\mathbf{k}) = \omega_c^2 + sk_\perp^2 + s_z k_z^2 \pm [s_1(k_x^2 - k_y^2)^2 + s_2 k_x^2 k_y^2]^{1/2} = \omega_c^2 + sk_\perp^2 + s_z k_z^2 \pm s_1 k_\perp^2\left[\cos^2 2\varphi \mp \frac{s_2^2}{4s_1^2}\sin^2 2\varphi\right]^{1/2}. \qquad (37)$$

Returning to formula (35), we note that the first δ-function describes the process of decomposition of the polarization vibration into two critical vibrations. This process has a threshold $\omega = 2\omega_c(T)$. To calculate the losses close to the threshold, we neglect the anisotropy in the x, y plane. Then

$$\Gamma_1(\omega)=\frac{Tv_0|V^{(3)}_{012}(0,0,0)|^2}{16\pi ss_z^{1/2}\omega^3}\sqrt{\omega^2-4\omega_c^2}. \quad (38)$$

The presence of such a threshold in the dielectric losses, the position of which depends strongly on the closeness to the transition point, points to the fact that we are dealing with a complex transition of the displacive type.

The second δ-function in formula (35) corresponds to the processes 0 + 1 → 2, which do not have a threshold. At small ω, regions of intersection or touching of the phonon branches contribute to the corresponding integrals. We shall confine ourselves to the main one of these—the region close to the critical minimum.

As a result, we obtain for $\omega \ll \omega_c$

$$\Gamma_2(\omega)=\frac{Tv_0|V^{(3)}_{012}(0,0,0)|^2}{32\pi^2 s_1 s_z^{1/2}\omega_c^2}F\left(\frac{\pi}{2},\sqrt{1-s_2^2/4s_1^2}\right) \quad (39)$$

where $F(\pi/2, k)$ is a complete elliptical integral of the first kind.

7. CONCLUSION

Thus, complex phase transitions constitute a broad class of phase transitions in crystals. Complex ferroelectrics are, evidently, the most convenient subject for experimental study. In these substances, the asymmetric phase arises at $T < T_c$ in a single-domain state, and the dielectric permittivity has a weak singularity analogous to the singularity in the specific heat, but the permittivity index differs from the specific heat index. The spontaneous polarization increases relatively slowly in the asymmetric phase, and its index is related to the index of the permittivity.

Examples of complex ferroelectrics are ammonium fluoroberyllate[15] and gadolinium molybdate.[16] The latter substance is an ionic crystal and the dielectric anomaly in it is weak. One may therefore hope that the transition in $Gd_2(MoO_4)_3$ is a displacive transition. In this connection, the observation of a threshold singularity in the dielectric losses in $Gd_2(MoO_4)_3$ is of interest.

The author thanks A. I. Larkin and A. M. Polyakov for useful discussions.

APPENDIX

We shall consider here the four-dimensional isotropic model, using which it is easy to see that the different three-tail functions behave differently as $k \to 0$, $\tau \to 0$.

As in Appendix 2 of [6]

$$H=\frac{1}{2}\sum_k(\tau+k^2)\eta_k^\alpha\eta_{-k}^\alpha+\frac{b}{4}\sum_{k_1+k_2+k_3+k_4=0}\eta_{k_1}^\alpha\eta_{k_2}^\alpha\eta_{k_3}^\beta\eta_{k_4}^\beta$$

k is a four-dimensional vector, and η^α are the components of the order parameter. The Green function $G^{-1}_{\alpha\beta}(k) = \delta_{\alpha\beta}(\tau + k^2)$. The effective interaction

$$\Gamma_{\alpha\beta\gamma\delta}(x)=\frac{\Gamma(x)}{3}(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})$$

$$\left(x=\ln\frac{k^2+\tau}{\Lambda^2}\right)$$

satisfies the equation

$$\Gamma(x)=\gamma-\frac{n+8}{3}\int_0^x dy\Gamma^2(y) \quad (A.1)$$

where γ is the dimensionless bare interaction. Solving (A.1), we obtain

$$\Gamma(x)=\gamma\Big/\left(1+\gamma\frac{n+8}{3}x\right).$$

The arbitrary three-point diagram $\mathcal{T}_{\alpha\beta}(x)$ can be represented in the form

$$\mathcal{T}_{\alpha\beta}(x)=\mathcal{T}_1(x)\delta_{\alpha\beta}+\mathcal{T}_2(x)\mathbf{l}\mathbf{Y}_{\alpha\beta}. \quad (A.2)$$

Here $\mathbf{Y}_{\alpha\beta}$ is a symmetric tensor with zero trace and $|\mathbf{l}| = 1$. For n = 2, we have $\mathbf{Y}\cdot\mathbf{l} = \hat{\sigma}_x l_x + \hat{\sigma}_z l_z$, and for n = 3, $\mathbf{Y}_{\alpha\beta}$ is the wave function of spin S = 2. The bare part of $\hat{\mathcal{T}}$ is $\delta_{\alpha\beta} + \mathbf{l}\cdot\mathbf{Y}_{\alpha\beta}$, and the exact equation has the form

$$\mathcal{T}_{\alpha\beta}(x)=\delta_{\alpha\beta}+\mathbf{l}\mathbf{Y}_{\alpha\beta}-\int_0 dy\mathcal{T}_{\mu\nu}(y)\mathcal{T}_{\mu\nu\alpha\beta}(y).$$

Using the equality $\mathbf{Y}_{\alpha\alpha} = 0$, we obtain

$$\begin{aligned}\mathcal{T}_1(x)&=1-\frac{n+2}{3}\int_0^x\mathcal{T}_1(y)\Gamma(y)\,dy,\\ \mathcal{T}_2(x)&=1-\frac{2}{3}\int_0^x\mathcal{T}_2(y)\Gamma(y)\,dy,\end{aligned} \quad (A.3)$$

whence it follows that

$$\begin{aligned}\mathcal{T}_1(x)&=\left(1+\gamma\frac{n+8}{3}x\right)^{-(n+2)/(n+8)},\\ \mathcal{T}_2(x)&=\left(1+\gamma\frac{n+8}{3}x\right)^{-2/(n+8)}.\end{aligned} \quad (A.4)$$

We also calculate the corresponding polarizabilities:

$$\Pi_{\alpha\beta}(x)=\Pi_1(x)\delta_{\alpha\beta}+\Pi_2(x)\mathbf{l}\mathbf{Y}_{\alpha\beta},$$

$$\Pi_1(x)=\int_0^x\mathcal{T}_1^2(y)\,dy\sim\left[\left(1+\gamma\frac{n+8}{3}x\right)^{(4-n)/(n+8)}-1\right],$$

$$\Pi_2(x)=\int_0^x\mathcal{T}_2^2(y)\,dy\sim\left[\left(1+\gamma\frac{n+8}{3}x\right)^{4/(n+8)}-1\right]. \quad (A.5)$$

Thus, for $\gamma x \gg 1$, we have for n = 2

$$\mathcal{T}_1(x)\sim x^{-2/5},\quad \Pi_1(x)\sim x^{1/5},$$
$$\mathcal{T}_2(x)\sim x^{-1/5},\quad \Pi_2(x)\sim x^{2/5},$$

and for n = 3

$$\mathcal{T}_1(x)\sim x^{-5/11},\quad \Pi_1(x)\sim x^{1/11},$$
$$\mathcal{T}_2(x)\sim x^{-2/11},\quad \Pi_2(x)\sim x^{4/11}.$$

[1] V. L. Indenbom, Kristallografiya 5, 115 (1960) [Sov. Phys.-Crystallogr. 5, 106 (1960)]; Izv. AN SSSR ser. fiz. 24, 1180 (1960).
[2] A. P. Levanyuk and D. G. Sannikov, Zh. Eksp. Teor. Fiz. 55, 256 (1968) [Sov. Phys.-JETP 28, 134 (1969)].
[3] L. P. Kadanoff et al., Rev. Mod. Phys. 39, 395 (1967); V. L. Pokrovskiĭ, Usp. Fiz. Nauk 94, 127 (1968) [Sov. Phys.-Usp. 11, 66 (1968)].
[4] A. M. Polyakov, Zh. Eksp. Teor. Fiz. 55, 1026 (1968); 57, 271 (1969) [Sov. Phys.-JETP 28, 533 (1969); 30, 151 (1970)].
[5] A. A. Migdal, Zh. Eksp. Teor. Fiz. 55, 1964 (1968) [Sov. Phys.-JETP 28, 1036 (1969)].

[6] A. I. Larkin and D. E. Khmel'nitskii, Zh. Eksp. Teor. Fiz. **56**, 2087 (1969) [Sov. Phys.-JETP **29**, 1123 (1969)].
[7] A. I. Larkin and S. A. Pikin, Zh. Eksp. Teor. Fiz. **56**, 1664 (1969) [Sov. Phys.-JETP **29**, 891 (1969)].
[8] V. G. Vaks and A. I. Larkin, Zh. Eksp. Teor. Fiz. **49**, 975 (1965) [Sov. Phys.-JETP **22**, 678 (1966)].
[9] L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR **96**, 469 (1954).
[10] A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **49**, 1304 (1965) [Sov. Phys.-JETP **22**, 901 (1966)].
[11] V. G. Vaks, Zh. Eksp. Teor. Fiz. **54**, 910 (1968) [Sov. Phys.-JETP **27**, 486 (1968)].
[12] B. Ya. Balagurov, V. G. Vaks and B. I. Shklovskiĭ, Fiz. Tverd. Tela **12**, 89 (1970) [Sov. Phys.-Solid State **12**, 70 (1970)].
[13] A. P. Levanyuk and V. G. Sannikov, Fiz. Tverd. Tela **12**, 2997 (1970) [Sov. Phys.-Solid State **12**, 2418 (1971)].
[14] L. D. Landau and E. M. Lifshitz, Table 7 in Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz,, M., 1963 (English transl. Pergamon Press, Oxford, 1965).
[15] B. A. Strukov, N. D. Gavrilova and V. A. Koptsik, Kristallografiya **6**, 780 (1961) [Sov. Phys.-Crystallogr. **6**, 625 (1962)].
[16] L. E. Gross, A. Fouskava, and S. E. Gummins, Phys. Rev. Lett. **21**, 812 (1968).

Translated by P. J. Shepherd
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