CONFERENCES AND SYMPOSIA

Phase transitions in ferroelectrics: some historical remarks

V L Ginzburg

Abstract. The 10th International Conference on ferroelectricty was held on 3 – 7 September, 2001 in Madrid, Spain. At a plenary session of the conference, a talk was delivered, whose content is presented in the present paper. The paper is primarily concerned with the work of V L Ginzburg and other Russian physicists on the theory of ferroelectric phenomena.

1. My talk is devoted to comments on the history of the creation of the theory of ferroelectric phenomena. I shall touch upon results, mostly of phenomenological nature, which are now well-known and are elucidated in many books (I shall mention here at least the excellent monograph by M Lines and A Glass [1]).

Therefore, the question immediately arises of why I have chosen such a subject for the talk. Answering this question, I shall note, first, that I myself had no intention to offer any communication for the present conference. However, when invited to do so, I felt I wished to attend an international conference on ferroelectricity at least once in my life.

The point is that I first took an interest in ferroelectric phenomena in 1945 and published a number of papers [2 – 7] on the subject, but not once did I have an opportunity to participate in such conferences. And when invited to the 6th such conference held in Kyoto (Japan) in 1985, I submitted a paper [8] mainly devoted to my own works [2 – 7].

Such were the conditions of life and work for most physicists in the Soviet Union in the years of 'cold war'. To somehow illustrate the conditions of our work, I shall mention the following fact. There was such a phrase in my paper [8]: "I cannot attend the present meeting and most probably will not be able to in the future". The editor of the Russian version discarded this phrase. I am happy to have lived to the downfall of the Communist regime nearly 10 years ago. Now people in Russia have the freedom of speech and migration. I mention it because the participants of this conference are mostly young people and they should not forget about the conditions of life under a totalitarian (Fascist or Communist) regime and, if needed, should defend democracy.

I would like to note that I am against priority disputes and generally forwarding the questions of priority. Everything is clear in this sphere from the corresponding publications, especially at the contemporary level of information exchange. That is why, mentioning some of my works in report [8] and below in this paper can only be justified by the fact that they were written rather long ago when Soviet physicists were unable to publish their works freely (suffice it to say that the *USSR Journal of Physics* stopped being published in 1947, and then it became practically impossible to publish papers in English for several years). I have no priority claims to anybody [1].

It is time, however, to proceed to the subject matter (I shall make use of my paper [8], but repetitions are inevitable).

2. The discovery of ferroelectricity in a sample of Rochelle salt may, although rather conditionally, be referred to 1920 [9] (see Ref. [1]). Much was clarified [10] within the decade to follow, but as far as I know, it was only in 1937 that Jaffe hypothesized the occurrence of phase transitions at Curie points (at $\Theta_1 = 255$ K and $\Theta_2 = 297$ K) in Rochelle salt [11]. In the ferroelectric region (i.e., at a temperature T lying between Θ_1 and Θ_2) the crystal is monoclinic, and outside this region it is orthorhombic.

Further, a phenomenological theory of the behavior of the Rochelle salt was developed [12, 13]. Since this salt is a complicated object and the general approach to the phase transition theory, known as the Landau theory [14], was not used, papers [12, 13] were not very general and transparent. Clarity and generality were reached as a result of the investigation of barium titanate ($BaTiO_3$). In 1944 Vul and Goldman found [15] that barium titanate ceramics showed a high dielectric permittivity ε which varied strongly with temperature and had a rather high maximum at $T \approx 400$ K. The polycrystalline nature of the samples and shortage of data veiled the fact that they were dealing with a new ferroelectric [2].

However, I understood that $BaTiO_3$ was a ferroelectric [2] and applied the Landau theory [14, 16] to describe its behavior; as the order parameter I chose the electric polarization P. It should be noted that the Landau theory of phase transitions is the mean (self-consistent) field theory, and in particularly simple cases it reduces to the Van-der-Waals and other constructions that had been well-known for a long time. The power of the Landau theory rests on its consistent use of the symmetry laws and the automatism of its

V L Ginzburg P N Lebedev Physics Institute,
Russian Academy of Sciences,
Leninskiĭ prosp. 53, 119991 Moscow, Russian Federation
Tel. (7-095) 135 85 70. Fax (7-095) 135 85 33
E-mail: ginzburg@lpi.ru

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[1] Unfortunately, various statements are sometimes far from reality. That is why I permit myself to note that although the author of several hundred papers and a number of innovations, I have never applied for any patents. I shall recall the fact, mentioned also in Ref. [8], that sometime in the fifties I gave evidence in court in the USSR, upon an order from the USA, concerning the employment of piezoelectric barium titanate sensors. On the basis of some agreement on juridical collaboration with the USSR, the USA government used my testimony, with reference to paper [2], to reject the claim of payment for some patents exploiting $BaTiO_3$.

[2] Paper [15] ends with a remark that the available "...facts, as well as the composition and structure of barium titanate do not allow it to be included in the group of ferroelectrics".

application. This was reflected in paper [2] which was submitted for publication on July 31, 1945. In this paper, the thermodynamic potential (more precisely, its density) was written in the form[3]:

$$\Phi = \Phi_0 + \alpha P^2 + \frac{\beta}{2} P^4 + \frac{\gamma}{6} P^6 - EP, \qquad (1)$$

where E is the electric field strength and the coefficients α, β, and γ depend on the temperature T.

The decomposition (1) is valid, generally speaking, only in the vicinity of the transition point Θ; we mean second-order transitions or first-order transitions that are close to the tricritical point [this point was earlier termed the critical Curie point; at this point, i.e., at $T = \Theta_{\text{tr}}$, the coefficient $\beta(\Theta_{\text{tr}}) = 0$ is equal to zero]. Far from the tricritical point Θ_{tr}, in the case of a second-order transition one may put $\gamma = 0$. In this case

$$\alpha(T) = \alpha'_{\Theta}(T - \Theta), \quad \beta = \beta_{\Theta}; \quad \alpha'_{\Theta} = \left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{T=\Theta} > 0 \qquad (2)$$

and at $T > \Theta$ in equilibrium we have a paraelectric phase [i.e., $P_0(T) = 0$], while at $T < \Theta$ spontaneous polarization occurs and

$$P_0^2 = -\frac{\alpha}{\beta} = \frac{\alpha'_{\Theta}(\Theta - T)}{\beta_{\Theta}}, \quad T < \Theta. \qquad (3)$$

The jump of the specific heat is

$$\Delta C_{\Theta} = \frac{\Theta}{\beta_{\Theta}} (\alpha'_{\Theta})^2. \qquad (4)$$

Taking into account that in equilibrium $\partial\Phi/\partial P = 0$, we obtain $E = 2\alpha P + 2\beta P^3$. In a weak field we have

$$P = P_0 + \frac{\varepsilon - 1}{4\pi} E$$

and, accordingly,

$$\begin{aligned} \alpha(T) &= \frac{2\pi}{\varepsilon - 1}, \quad T > \Theta; \\ \alpha(T) &= -\frac{\pi}{\varepsilon - 1}, \quad T < \Theta. \end{aligned} \qquad (5)$$

Here in $\varepsilon(T)$ a certain term ε_0 not connected with the transition is in fact neglected; assuming also that $\varepsilon \gg 1$, by virtue of (2) we obtain

$$\begin{aligned} \varepsilon(T) &= \frac{2\pi}{\alpha'_{\Theta}(T - \Theta)}, \quad T > \Theta; \\ \varepsilon(T) &= \frac{\pi}{\alpha'_{\Theta}(\Theta - T)}, \quad T < \Theta. \end{aligned} \qquad (6)$$

Thus, we arrive at the Curie – Weiss law and at the so-called 'law of two' according to which $\varepsilon(T > \Theta)/\varepsilon(T < \Theta) = 2$ for the same value of $|\Theta - T|$.

In paper [2] we presented a number of other results, in particular, those near first-order transitions close to second-

order transitions; moreover, some experimental data concerning $BaTiO_3$ and KH_2PO_4 type ferroelectrics were discussed in Ref. [2]. It was also noted that above the Curie point $BaTiO_3$ showed, of course, no piezoeffect. But in the ferroelectric phase it must be observed, and paper [2] pointed to the corresponding possibilities for tetragonal or orthorhombic pyroelectric (polar) phases (i.e., at $T < \Theta$; what was this phase in $BaTiO_3$ was then unknown). I do not want to dwell here in more detail on the content of paper [2] because it was published in English as well.

3. The main shortfall of paper [2] was that it treated, in fact, the one-dimensional case alone where the spontaneous polarization P_0 was aligned in only one direction. This approach is pertinent in the consideration of the properties of Rochelle salt or KH_2PO_4 type substances possessing preferred axes already outside the ferroelectric phase. In the case of ceramics, i.e., a polycrystal, for which the ferroelectric properties of $BaTiO_3$ were discovered [15], my consideration [2] with a single order parameter P was also natural. But in application to $BaTiO_3$ single crystals a more general approach with the vector parameter **P** was needed. How to do it within the Landau theory is quite clear (see, for example, Refs [16, 17]). Why I did not do it at once can only be explained by the fact that my interest in this problem was insufficient and I was occupied by quite different problems. But after the appearance of new experimental data [18 – 20] I eventually did it [3, 4], although regretfully with some delay (paper [3] was submitted for publication on July 7, 1948 but already could not be published in English).

Specifically, in Refs [3, 4] I used the thermodynamic potential

$$\begin{aligned} \Phi = {}&\Phi_0 + \alpha(P_x^2 + P_y^2 + P_z^2) + \frac{\beta_1}{2}(P_x^4 + P_y^4 + P_z^4) \\ &+ \beta_2(P_x^2 P_y^2 + P_x^2 P_z^2 + P_y^2 P_z^2) + \frac{1}{2} s_{11}(\sigma_{xx}^2 + \sigma_{yy}^2 + \sigma_{zz}^2) \\ &+ s_{12}(\sigma_{xx}\sigma_{yy} + \sigma_{xx}\sigma_{zz} + \sigma_{yy}\sigma_{zz}) + \frac{1}{4} s_{44}(\sigma_{xy}^2 + \sigma_{xz}^2 + \sigma_{yz}^2) \\ &- \gamma_1(\sigma_{xx}P_x^2 + \sigma_{yy}P_y^2 + \sigma_{zz}P_z^2) \\ &- \gamma_2[\sigma_{xx}(P_y^2 + P_z^2) + \sigma_{yy}(P_x^2 + P_z^2) + \sigma_{zz}(P_x^2 + P_y^2)] \\ &- 2\gamma_3(\sigma_{xy} P_x P_y + \sigma_{xz} P_x P_z + \sigma_{yz} P_y P_z) \\ &- (E_x P_x + E_y P_y + E_z P_z), \qquad (7) \end{aligned}$$

where $\mathbf{P} \equiv \{P_i\} = \{P_x, P_y, P_z\}$ is the polarization vector (the order parameter) and σ_{ik} is the stress tensor.

In equilibrium $E_i = \partial(\Phi + E_k P_k)/\partial P_i$, and (7) implies the relation for E_i, P_i, and σ_{ik}. At $T < \Theta$, when $\alpha < 0$, solutions are possible that correspond to tetragonal and orthorhombic symmetries. Furthermore, in Ref. [3] the coefficients β_1 and β_2 were so chosen that the absolute minimum of Φ corresponded to the tetragonal structure in accord with the experimental data [18]. I shall not present formulas here, for they coincide with those available in all modern courses (see Refs [1, 17]).

Unfortunately, I do not remember why I did not include in Refs [3, 4], unlike [2], terms of the order of P^6. Therefore, the solutions corresponding to the orthorhombic phase were not found and first-order transitions close to the tricritical point were not considered. This shortfall was partially offset in papers by Devonshire [21 – 23]. The potential used in those papers differed from (7) only by addition of the term $(1/6)\xi'(P_x^6 + P_y^6 + P_z^6)$. Meanwhile, when writing terms of

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[3] To be absolutely precise, in Ref. [2] expression (1) with $\gamma = 0$ was written down. Later, however, it was found necessary to add the term $(\gamma/6)P^6$ in case the transition was close to the tricritical point Θ_{tr}.

the order of P^6, one should use the general expression $(P^2 = P_x^2 + P_y^2 + P_z^2)$:

$$\Phi_6(P) = \frac{1}{6}\gamma_1 P^6 + \gamma_2 \left[P_x^4(P_y^2 + P_z^2) + P_y^4(P_x^2 + P_z^2) \right.$$
$$\left. + P_z^4(P_x^2 + P_y^2) \right] + \gamma_3 P_x^2 P_y^2 P_z^2. \qquad (8)$$

This was later done by Kholodenko and Shirobokov [24]. Incidentally, in Ref. [21] Devonshire referred to my paper [2], and therefore he might have paid attention to the Landau theory, but he did not and hence obtained only a particular result. Paper [21] was submitted for publication on July 26, 1949, i.e., a year later than [3]. At the same time, as has been said, in Ref. [17] the role of P^6-order terms was at least partially allowed for, and the experimental data, in particular, paper [25], were also used and taken into account much more widely than in [3]. So, I do not in the least want to diminish the value of Devonshire's works.

4. Quite a significant role in the understanding of the mechanism of ferroelectric and some other transitions has been played by the so-called 'soft mode' concept. It consisted in the following. Under second-order transitions and first-order transitions close to the tricritical point, the frequency of one or several normal crystal lattice modes tends to zero or strongly decreases. For real crystals, however, the picture may be very complicated. The 'soft mode' concept has set in gradually as a result of a number of experimental and theoretical studies. It would be interesting to see a comprehensive analysis of the history of this question. I can only make some comments on this issue. As far as I know, Landsberg and Mandelstam [26] were the first to pay attention to the 'soft mode' in 1929 during the study of combinational (Raman) scattering of light in quartz near the $\alpha \rightleftarrows \beta$ transition. It turned out that the line of 207 cm^{-1} (at room temperature) extends and smears out with rising temperature, and disappears altogether in β-quartz (i.e., a $T > \Theta = 846$ K).

Later on it became clear [27–29] that as the temperature grows, the frequency of this line falls sharply. These facts were taken into account by A P Levanyuk and me in the paper [30] published in 1960 and devoted to the spectral composition of light scattered near second-order phase transition points. In that paper we spoke of the 'soft mode', i.e., the disappearance of the frequency of the oscillation responsible for the transition, as a well-known concept (the corresponding quotation is presented also in Ref. [8]).

I would not like, however, to dwell in more detail on light scattering and 'soft modes', the more so as I can refer in this connection to the reviews [31, 32]. Now I shall note that the 'soft mode' had appeared explicitly already in papers [3, 4], that is, in 1949. Since papers [3, 4] were not translated into English, I shall present, although it has already been done in Ref. [8], a rather long quotation: "Let us also consider the dispersion of the dielectric constant of barium titanate. This problem is much more complicated than the one considered above because it does not admit a purely thermodynamical treatment. It can, in fact, be solved only through investigation of the lattice mode. Some statements and dispersion estimates can however be made without such a consideration. For simplicity we shall restrict ourselves to the case of a field aligned parallel to a spontaneous moment, i.e., along the corresponding axis of the cube". Next, comparing the static expression $2\alpha P + 2\beta_1 P^3 = E$ (here P is polarization along the indicated axis) with the equation of motion for an anharmo-

nic oscillator

$$m\ddot{\xi} + r\dot{\xi} + k\xi + s\xi^3 = eE, \qquad (9)$$

we come to the equation [for the field $E = E_0 \exp(i\omega t)$]

$$\mu\ddot{P} + \nu\dot{P} + \alpha P + \beta_1 P^3 = \frac{E_0}{2}\exp(i\omega t),$$
$$P = eN\xi, \qquad \mu = \frac{m}{2e^2 N}, \qquad \nu = \frac{r}{2e^2 N}. \qquad (10)$$

From this, for the dielectric constant ε we obtain the expressions

$$\left.\begin{array}{l} \varepsilon = \dfrac{2\pi}{\alpha + i\omega\nu - \omega^2\mu}, \qquad T > \Theta, \\[4mm] \varepsilon = \dfrac{2\pi}{-2\alpha + i\omega\nu - \omega^2\mu}, \qquad T < \Theta. \end{array}\right\} \qquad (11)$$

From (11) and (3) it is clear that the eigenfrequency ω_i of the mode in question near a second-order transition is as follows:

$$\omega_i^2 = \frac{\alpha}{\mu} = \frac{\alpha'_\Theta}{\mu}(T - \Theta), \qquad T > \Theta,$$
$$\omega_i^2 = \frac{2\alpha}{\mu} = \frac{2\alpha'_\Theta}{\mu}(\Theta - T), \qquad T < \Theta. \qquad (12)$$

Obviously, at the transition point $\omega_i = 0$, and ω_i is precisely the 'soft mode'.

In Ref. [3] I present an estimate of the dispersion which agrees qualitatively with the measurements [33] published a year before. It should be noted that in Refs [3, 4] expressions (12) were not written. It seems to me that they follow from (11) in an obvious way, provided one knows a usual formula of the type $\varepsilon = \varepsilon_\infty + A/(\omega_0^2 - \omega^2 - i\gamma\omega)$. But maybe I am wrong and the consideration of the soft mode in Refs [3, 4] was indeed somewhat vague ("obscurely worded, even with the benefit of hindsight", as was noted by Cochran [34]). I wrote about it in some more detail in Ref. [8].[4] Here, I shall restrict myself to the remark that in any case I do not agree with the opinion (see [1], Sec. 1.1 and [35]) that the 'soft mode' concept was 'introduced by Anderson [36] and Cochran [37] in 1960' (this is a quotation from Ref. [35]). The papers by Cochran [37, 38] are indeed valuable and more extensive than the corresponding material in Refs [3, 4], but they appeared 10 years later. As concerns the paper by Anderson [10], its citations are 'adapted by repetition'. As was justly noted by Cochran [34] in respect of the report by Anderson [36], "contrary to what many who have cited this paper believe, it is primarily not at all about soft modes!" To make it more clear, I shall add that the book in which Anderson's paper [36] appeared was issued only in Russian, and I am sure that those who cited it had never seen the book (for some more details see Ref. [8]).

5. Report [8] was written in 1985, that is, before the discovery of high-temperature superconductivity (HTSC) (1986–1987). But the problem itself has been under discussion since 1964 (for a short history of the question see Refs [39, 40]). A possible relation between HTSC and ferroelectricity had frequently been mentioned even before 1986 (see references in [8]). In this connection, obviously, in the

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[4] Note that in the English version of paper [8] the editor changed the phrase in my polemics with Cochran without my knowledge.

invitation to make the report [8], I was asked to elucidate this relation. For this reason, the last section in paper [8] was entitled "Ferroelectricity, soft modes and the problem of high-temperature superconductivity". One could hope that now, 15 years after the discovery of HTSC, the question should have become sufficiently clear. But this is not so, and even the very nature (mechanism) of HTSC in cuprates remains unclear. It is however difficult to doubt that the electron-phonon interaction also plays a significant role in cuprates [41], to say nothing of the recently discovered superconductivity in MgB$_2$ [42]. That is why it seemed to me to be relevant to repeat briefly what was said in Ref. [8] in respect of a certain relation between HTSC and ferroelectricity.

The appearance of a ferroelectric transition is often (and not without reason) associated with the so-called polarization 'catastrophe' (see, e.g., Ref. [43], Ch. 14). This 'catastrophe' is due to the account of the difference between the mean macroscopic electric field **E** and the effective or acting field **E**$_{\rm eff}$. Restricting the consideration to an isotropic body or a cubic crystal for simplicity, one can put

$$\mathbf{E}_{\rm eff} = \mathbf{E} + f\mathbf{P}. \tag{13}$$

In a solid body and liquids, in some models the coefficient $f = 4\pi/3$, and thus the well-known expression $\mathbf{E}_{\rm eff} = \mathbf{E} + (4\pi/3)\mathbf{P}$ holds. But this is undoubtedly a model result, and for example in a rarefied plasma we have $f = 0$.

Using (13) and the expression

$$\mathbf{P} = \frac{\varepsilon - 1}{4\pi}\,\mathbf{E} = \chi N\mathbf{E}_{\rm eff}, \tag{14}$$

where χ is the polarizability of the considered dipoles and N is their concentration, we obtain

$$\varepsilon = 1 + \frac{4\pi\chi N}{1 - f\chi N}, \tag{15}$$

whence

$$\frac{\varepsilon - 1}{1 + (\varepsilon - 1)f/(4\pi)} = 4\pi\chi N. \tag{16}$$

For $f = 4\pi/3$ this implies the well-known Clausius – Mossotti or Lorenz – Lorentz formula (for more details see Ref. [44])

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\,\chi N \tag{17}$$

(more precisely, the Lorenz – Lorentz formula is expression (17) with $\varepsilon = n^2$, where n is the refractive index).

From Eqn (15) it is obvious that as $f\chi N \to 1$, the dielectric constant (permittivity) $\varepsilon \to \infty$. This is precisely what we call the polarization 'catastrophe' (see also Ref. [45]). For $f\chi N > 1$, according to (15) we already have $\varepsilon < 0$ (we do not pay attention to the summand 1 which should have been replaced by a certain quantity ε_0). But for $f\chi N > 1$, i.e., $\varepsilon < 0$, the lattice becomes unstable, and thus the polarization 'catastrophe' corresponds to a phase transition with the appearance of a spontaneous polarization P_0.

As is known (see, e.g., Ref. [46]), with allowance for spatial dispersion ε in (15) this is the longitudinal dielectric permittivity $\varepsilon_{\rm l}(\omega, \mathbf{k})$ taken for $\omega = 0$, $\mathbf{k} = 0$ (the field $\mathbf{E} = \mathbf{E}_0 \exp[\mathrm{i}(\omega t - \mathbf{k}\mathbf{r})]$ is meant). Given this, the lattice in a homogeneous field (i.e., for $k = 0$) is stable provided that

$$\varepsilon_{\rm l}(0, 0) \geqslant 1. \tag{18}$$

But if $k \neq 0$ (and, say, $k \gg 1/L$, where L is the body size), the stability condition has the form (see Refs [39, 40] and the literature cited there)

$$\frac{1}{\varepsilon_{\rm l}(0, k)} \leqslant 1, \tag{19}$$

that is, the lattice is stable both for $\varepsilon_{\rm l}(0, k) \geqslant 1$ and

$$\varepsilon_{\rm l}(0, k) < 0, \qquad k \neq 0. \tag{20}$$

Thus we see that for $k \neq 0$ the polarization 'catastrophe' does not occur and negative $\varepsilon_{\rm l}$ values are possible. But this is just what is important for the theory of superconductivity because for $\varepsilon_{\rm l} < 0$ the Coulomb law $V = e^2/(\varepsilon_{\rm l} r)$ corresponds not to repulsion, but to attraction between like charges (specifically, electrons). Precisely this attraction is needed for the formation of Cooper pairs and superconductivity.

For the sake of clearness, we give here a somewhat vulgarized explanation. But the fact is that for the appearance of superconductivity it is in any case sufficient that the region with $\varepsilon_{\rm l}(0, k) < 0$ appear for large $k \sim k_{\rm F}$, where $k_{\rm F}$ is the value of k corresponding to the Fermi surface. It should be noted that negative values of $\varepsilon_{\rm l}(0, k)$ for a wide range of k values are not only possible but actually exist for a whole number of systems [47] owing to the phonon contribution in $\varepsilon_{\rm l}$. One way or another, the HTSC problem, as well as the hypothetical and desired RTSC (room-temperature superconductivity), is closely related to the search for substances with $\varepsilon_{\rm l}(0, k) < 0$ for the highest possible values of $|\varepsilon_{\rm l}(0, k)|$. It is necessary to take into account the difference between $\mathbf{E}_{\rm eff}$ and $\mathbf{E}$. What is possible in this respect, remains unclear; the current state of the problem is outlined in Ref. [41]. Here I only wanted to point out a certain relation between the conditions of the appearance of ferroelectricity and superconductivity 'in the language' of dielectric permittivity $\varepsilon_{\rm l}(0, k)$.

6. As has already been emphasized, the Landau theory of phase transitions [14, 16] is the theory of a self-consistent (mean) field, i.e., it disregards fluctuations in calculations of the corresponding quantities [i.e., the spontaneous polarization P_0; see (3)]. However, when fluctuations are small, they can be calculated in a usual manner using the Landau theory, and the thermodynamic potential (1) referring to the spatially homogeneous case should be supplemented with the gradient term, i.e., Φ should be written in the form (we assume $E = 0$)

$$\Phi(P(\mathbf{r})) = \Phi_0 + \alpha P^2 + \frac{\beta}{2}\,P^4 + \frac{\gamma}{6}\,P^6 + \delta(\nabla P)^2. \tag{21}$$

Here, obviously, the order parameter P is the component of the vector **P** along the preferred axis. Using the expansion

$$\Delta P \equiv P - P_0 = \sum_{\mathbf{k}} P_{\mathbf{k}} \exp(\mathrm{i}\mathbf{k}\mathbf{r}) \tag{22}$$

to calculate the fluctuations, we obtain in a usual manner (see, for example, Ref. [16] Sec. 116, 146, and [5, 8])

$$\overline{(\Delta P)^2} = \frac{k_{\rm B}\Theta}{8\pi\delta}\sqrt{\frac{2|\alpha|}{\delta}} = \frac{k_{\rm B}\Theta^{3/2}(\alpha'_\Theta)^{1/2}\tau^{1/2}}{4\sqrt{2}\,\pi\delta^{3/2}}, \tag{23}$$

where k_B is the Boltzmann constant, and we are dealing with a typical second-order phase transition [$\gamma = 0$, $\beta = \beta_\Theta$, $\alpha = \alpha'_\Theta(T - \Theta)$, $\tau = (\Theta - T)/\Theta$]; the temperature-dependent part $\overline{(\Delta P)^2}$ is singled out, where the bar means statistical averaging.

The fluctuations are small if

$$\overline{(\Delta P^2)} \ll P_0^2 = \frac{\alpha'_\Theta(\Theta - T)}{\beta_\Theta} \,. \tag{24}$$

From (23), (24) we can see that the fluctuations are small until

$$\tau = \frac{\Theta - T}{\Theta} \gg \tau_0 = \frac{k_B^2 \Theta \beta_\Theta^2}{32\pi^2 \alpha'_\Theta \delta^3} \,, \tag{25}$$

where τ_0 is determined from the condition $\overline{(\Delta P)^2} = P_0^2 = \alpha'_\Theta \Theta \tau_0 / \beta_\Theta$. We note that a condition of the type (25) can also be obtained in a somewhat different but, in fact, coincident way (see Refs [48] and [16], Sec. 146). In Refs [7, 8] the expression for τ_0 is also presented which includes a jump of specific heat ΔC in the transition [see (4)] and a certain correlation radius $r = [\delta/(2\alpha'_\Theta \Theta)]^{1/2}$. The corresponding expression is useful in the analysis of the question of particular transitions. Some time ago such an analysis [7] (see also Refs [5, 8]) showed that the critical region [the region near the transition point, in which condition (25) is violated] was not yet established in the case of ferroelectrics. There are some reasons for this. Unfortunately, I am unaware of the current state of the problem and shall not therefore repeat here some remarks contained in Refs [7, 8]. I shall only point out that of particular interest from the point of view of observation of critical phenomena are, on the one hand, liquid-crystal ferroelectrics (in this case, complications due to deformation and stress are probably absent) and, on the other hand, quasi-two-dimensional ferroelectrics, i.e., thin ferroelectric films. It is a known fact that in the quasi-two-dimensional case fluctuations are generally much greater than those in three-dimensional systems.

7. Studies in the field of solid state physics and, in particular, ferroelectricity and related phenomena have been traditionally distinguished in the USSR and now in Russia. The corresponding references have partially been given above (see Refs [2–8, 10, 15, 17, 20, 24, 26, 30, 31, 45, 48]). I shall also mention monographs [49–51]. At the same time, in the preceding sections of the report attention was concentrated only on my own works. As concerns the early period (from 1945 to approximately 1960), this can be understood and I believe is justified by the essence of the matter. However, later on I was not systematically engaged in ferroelectric research and am a co-author of only three papers [6–8]. Of course, in my paper [8] and above in this text I did not in the least claim the elucidation of the development of ferroelectric studies after, say, 1960. But now it seems reasonable to enumerate at least briefly those later Russian papers in which significant results were reported [5].

In the first place I have to mention the work by Indenbom [52] who paid attention to improper ferroelectrics. In such substances, the order parameter is not the electric polarization **P**, but some other physical quantities (along with Ref. [52], see also [17] Sec. 20 and [51] Ch. 4). The subject of

Ref. [52] was substantially developed by Levanyuk and Sannikov [53]. The same authors [54] developed the theory of ferroelectric transitions that proceed with the participation of an intermediate incommensurate phase (for more details see, e.g., Ref. [51]). In the case of improper phase transitions, transitions with the participation of incommensurate phases, and some other (so-to-say nontrivial) transitions the Landau theory [14, 16] works with all its power and one cannot avoid using it.

Incommensurate phases and the corresponding transitions are considered in a large number of papers; this is a whole field of research [55, 56], and it would be out of place and simply impossible to dwell on it here. In what follows I shall restrict myself to mentioning the first, as far as I know, consideration of the domain structure in ferroelectrics [57]. Since I have long been unaware of the corresponding literature, I would only like to note that some papers on liquid-crystal ferroelectrics (see, e.g., Ref. [58]) and ferroelectric thin films [59, 60] have recently attracted attention. The fact that surface (two-dimensional or quasi-two-dimensional) ferroelectricity and surface ferromagnetism and superconductivity are possible has long been noticed [61][6]. However, it is only recently that all such surface phenomena has been given serious consideration.

Concluding, I shall mention the studies of ferrotoroics (the term was introduced by D G Sannikov). Alongside the well-known magnetization **M** and electric polarization **P** and the related magnetic and electric dipole moments $\mathbf{m} = \int \mathbf{M}\, dV$ and $\mathbf{p} = \int \mathbf{P}\, dV$, a substance (or generally any system of charges and currents) is characterized by the density **T** of toroidal moment and the toroidal dipole moment $\mathbf{t} = \int \mathbf{T}\, dV$. (True, the density **T** is normally called simply the toroidal moment, the same as the magnetization is sometimes referred to as the magnetic moment.) Given this, we have

$$\mathbf{j} = c\,\mathrm{rot}\,\mathbf{M} + c\,\mathrm{rot}\,\mathrm{rot}\,\mathbf{T}\,, \tag{26}$$

where **j** is the current density in a nonconducting system.

Until recently, the possibility of the existence of a toroidal moment **T** was ignored. Now it is obviously not the case, and the moment **T** is mentioned even in text books (see, e.g., Ref. [63] Ch. 7; there and in Refs [64–66] some other literature is also cited). The toroidal dipole moment is defined by the expression

$$\mathbf{t} = \int \mathbf{T}\, dV = \frac{1}{10\,c} \int \left\{(\mathbf{j}\,\mathbf{r})\mathbf{r} - 2r^2 \mathbf{j}\right\} d\mathbf{r}$$

$$= \frac{1}{10\,c} \sum_i e_i \left\{(\mathbf{v}_i\,\mathbf{r}_i)\mathbf{r}_i - 2r_i^2 \mathbf{v}_i\right\}, \tag{27}$$

where the second expression is written down for point-like charges with

$$\mathbf{j} = \sum_i e_i \mathbf{v}_i\, \delta(\mathbf{r} - \mathbf{r}_i)\,;$$

for comparison we recall that under the same conditions the electric dipole moment is

$$\mathbf{p} = \int \rho \mathbf{r}\, d\mathbf{r} = \sum_i e_i \mathbf{r}_i$$

[5] In preparation of this material I was assisted by D G Sannikov, I wish to thank him sincerely for this and for the comments he made on reading the manuscript.

[6] I cannot guarantee that surface ordering of ferromagnetic, antiferromagnetic, and ferroelectric types has not been mentioned earlier. Surface superconductivity was discussed in Ref. [62].

(this moment is independent of the choice of the origin provided that $\sum_i e_i = 0$).

The physical meaning of the toroidal dipole moment is particularly clear when a toroid with current (a solenoid rolled up as a torus) is considered. For such a toroid, the moment is $\mathbf{t} \neq 0$ and is perpendicular to the toroid plane, whereas $\mathbf{p} = 0$ and $\mathbf{m} = 0$. Inside the toroid, the magnetic field is $\mathbf{H} \neq 0$ and outside $\mathbf{H} = 0$ (we mean, of course, the simplest case when the toroid is not charged and does not carry an azimuthal current).

The transformation properties of $\mathbf{T}$ are the same as those of $\mathbf{j}$, that is, $\mathbf{T}$ is a polar vector. Substances with $\mathbf{P} = 0$ and $\mathbf{M} = 0$, but with $\mathbf{T} \neq 0$ represent a certain special class of substances. Of course, 'mixed' cases are also possible when not only $\mathbf{T}$, but $\mathbf{P}$ and (or) $\mathbf{M}$ are not equal to zero either. As has been mentioned above, substances with $\mathbf{T} \neq 0$ can be referred to as ferrotoroics. To the best of my knowledge, they were first considered in paper [64][7] and then were investigated in Refs [65, 66].

Looking back at the 56 years that have passed since the discovery of ferroelectricity in barium titanate and the appearance in press of my paper [2], I clearly see how much has been done during these years. I regret that I did not take an active part in the corresponding research. But as is well-known, one cannot do the impossible. There is every reason to assume that further advances in the studies of ferroelectrics, ferroelastics, and ferrotoroics will bring many interesting results. I personally think, as has already been pointed out, that especially noteworthy are liquid crystals (liquid-crystal ferroelectrics) and quasi-two-dimensional (surface) effects and, in particular, surface ferroelectricity. Ferrotoroics may also surprise us.

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[7] In Ref. [64] we were interested in ferrotoroics particularly in connection with the possible existence of superdiamagnetics. This issue now remains unclear. Some model arguments show that nonmagnetic ferrotoroics are good candidates as substances with a large diamagnetism (superdiamagnetism).

[8] This book does not elucidate the history of ferroelectric research, but gives a list of corresponding literature, mostly in Russian.\

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