

Theoretical investigations of the ferroelectric transition

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Abstract. The paper presents a historical review of theoretical concepts regarding the nature of the ferroelectric transition in crystals with a perovskite structure. We discuss Ginzburg’s phenomenological theory, including the idea of the soft phonon mode as a reason for the ferroelectric transition. The role played by the dipole–dipole interaction in softening the optical phonon mode is considered in the framework of the theory of lattice dynamics. The experimental data and theoretical results are presented that prove that the ferroelectric transition in perovskite crystals is due to the soft mode and is a displacement-type transition.

1. Introduction

This report can be considered a historical review of the evolution of theoretical concepts regarding the nature of the ferroelectric transition in ion crystals. The material presented is mainly based on reviews [1–3] published earlier in *Physics–Uspekhi*. Of course, the reviews of ferroelectricity published in *Uspekhi* are more numerous than the references given above, and we do not limit ourselves to presenting reviews [1–3]. Nor do we limit our consideration to long-known facts and theories concerning ferroelectricity. Instead, we consider some problems concerning the physics of ferroelectrics that have not been solved yet. Nevertheless, we start by considering the accepted phenomenological theory of ferroelectricity suggested by Ginzburg [1, 4] more than 60 years ago, which is still efficiently used.

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2. Phenomenological and model theories of ferroelectricity

The transition to the ferroelectric state is related to the origin of spontaneous electric polarization in a system, which is usually associated with its dipole moment. Ginzburg suggested writing the free energy of a ferroelectric in accordance with the Landau general theory of phase transitions in the form

$$\begin{aligned}
 F(T, \eta, P) = & \frac{1}{2} C_{11}(\eta_{11}^2 + \eta_{22}^2 + \eta_{33}^2) \\
 & + C_{12}(\eta_{22}\eta_{33} + \eta_{33}\eta_{11} + \eta_{11}\eta_{22}) + a_1(P_1^2 + P_2^2 + P_3^2) \\
 & + a_{11}(P_1^4 + P_2^4 + P_3^4) + a_{12}(P_1^2P_2^2 + P_1^2P_3^2 + P_2^2P_3^2) \\
 & + a_{111}(P_1^6 + P_2^6 + P_3^6) + g_{11}(\eta_{11}P_1^2 + \eta_{22}P_2^2 + \eta_{33}P_3^2),
 \end{aligned} \tag{2.1}$$

where C_{ij} are the elastic constants, η_{ij} is the stress tensor, and \mathbf{P} is the polarization vector. The free energy is expanded into a series, up to the sixth power, in the polarization. The last summand is responsible for a relation between the crystal tensions and the polarization. In the simplest case where tension effects are neglected, we can express the free energy as

$$F(T, P) = a_1P^2 + a_{11}P^4 + a_{111}P^6. \tag{2.2}$$

All the coefficients in (2.1) and (2.2) for the free energy depend on the temperature. Nevertheless, most of them are usually considered temperature independent in calculations. An important part of the theory is the temperature dependence of the coefficient a_1 , which is given by

$$a_1 = \alpha(T - T_c), \tag{2.3}$$

where α is a positive constant and T_c is the temperature of the system transition into the ferroelectric state. At $T > T_c$, the term quadratic in P is positive and the free energy, as a function of polarization, has a single minimum at $P = 0$. At $T < T_c$, the quadratic summand is negative and the thermodynamic potential has two minima at $P = \pm P_0$, where $P_0 =$

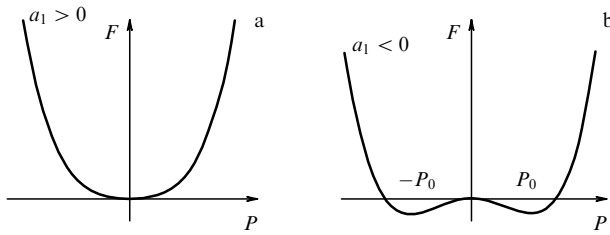


Figure 1. Free energy F of a ferroelectric as a function of polarization P for $T \geq T_c$ (a) and $T \leq T_c$ (b).

$\sqrt{-a_1/(2a_{11})}$ is the equilibrium polarization (see Fig. 1). The relation for F describes a second-order phase transition for $a_{11} > 0$ and a first-order phase transition for $a_{11} < 0$.

In problems with a spatially nonuniform polarization, free energy (2.1) may include a polarization gradient summand. Equation (2.1) may also include an external electric field \mathbf{E} :

$$F(T, \mathbf{P}) = a_1 \mathbf{P}^2 + a_{11} \mathbf{P}^4 - \mathbf{P} \mathbf{E}. \quad (2.4)$$

In equilibrium, the condition $\delta F / \delta P = 0$ implies

$$2a_1 \mathbf{P} + 4a_{11} \mathbf{P}^3 = \mathbf{E}. \quad (2.5)$$

In a weak field, we can write the relation

$$\mathbf{P} = \mathbf{P}_0 + \frac{\varepsilon - \varepsilon_\infty}{4\pi} \mathbf{E}, \quad (2.6)$$

where ε is the total static dielectric constant and ε_∞ is the high-frequency dielectric constant due to excited electron shells. From (2.5) and (2.6), we obtain the Curie–Weiss law for ε at $T \geq T_c$:

$$\varepsilon \approx \frac{2\pi}{\alpha(T - T_c)}, \quad (2.7)$$

according to which the dielectric constant should tend to infinity in the phase transition into the ferroelectric state. In the framework of the phenomenological approach, relation (2.5) was generalized by Ginzburg to the case of an alternating field [4]:

$$\mu P'' + \nu P' + a_1 P + 2a_{11} P^3 = \frac{1}{2} E_0 \exp(i\omega t). \quad (2.8)$$

The first two summands in (2.8) include time derivatives of the polarization and can be respectively written as $-\omega^2 P$ and $i\omega P$. Hence, at $T \geq T_c$, we obtain the dielectric function

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{2\pi/\mu}{\omega_1^2 - \omega^2 + i(v/\mu)\omega}, \quad (2.9)$$

where

$$\omega_1^2 = \frac{a_1}{\mu}. \quad (2.10)$$

Expression (2.9) is the standard dispersion relation, from which, in particular, the Liddén–Saks–Teller formula can be derived:

$$\frac{\varepsilon(0)}{\varepsilon_\infty} = \frac{\omega_1^2}{\omega_T^2}, \quad (2.11)$$

where the frequencies of the longitudinal ω_L and transverse ω_T excitations in the system respectively determine a zero and a pole of $\varepsilon(\omega)$. It follows from Eqns (2.9) and (2.11) that $\omega_L = \omega_i$, and Eqns (2.3) and (2.10) imply that the transverse excitation should exist in ferroelectrics, the so-called soft mode at the frequency that tends to zero as the temperature approaches T . The other situation is also possible, in which the properties of the ferroelectric system are determined not by an oscillating but by a relaxation mode. Then in (2.8) we should neglect the second derivative of P and write the dielectric function as

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{2\pi/a_1}{1 + i\omega\tau}, \quad (2.12)$$

where

$$\tau = \frac{\nu}{a_1} \approx \frac{1}{T - T_c} \quad (2.13)$$

is the relaxation time. The result obtained means that the relaxation time tends to infinity near the transition.

We do not thoroughly consider the phenomenological Ginzburg theory and the results that follow from it, because there are numerous reviews and monographs in this field (see, e.g., Refs [5, 6]). Recently, Bratkovsky and Levanyuk [7] presented a review of theoretical investigations in the framework of the Ginzburg theory for thin ferroelectric films and nanostructures of various types. In what follows, we mainly discuss theoretical problems concerning the nature of ferroelectricity itself and the reasons for its appearance in crystals.

As was mentioned above, the anomalous behavior of the low-frequency dielectric function in a ferroelectric phase transition, which is related to the presence of a ‘soft’ transverse optical mode in a system, was first mentioned by Ginzburg [1, 4]. Because no other low-energy transverse modes except phonons are present in ion crystals, it is natural to ascribe the lattice distortion in the ferroelectric transition to the loss of stability by one of the lattice normal vibrations. Later, Cochran [8, 9] presented the ferroelectric transition problem as just a problem of the loss of the lattice dynamics stability.

Another possibility of the arising ferroelectric instability is related to the presence of ions with a negative individual rigidity at the central (symmetric) position in the paraelectric phase. This means that the potential in which such an ion would move at fixed equilibrium positions of the rest lattice ions has several local minima shifted from the symmetric position. In this case, the phase transition to the ferroelectric state is related to the ion ordering in one such equivalent minimum and an anomalous system behavior may be observed for the relaxation processes near the point of transition to the ferroelectric state.

Experimental results show that there are two definite groups of ferroelectrics. In one of them (displacement-type ferroelectrics), the ferroelectric state arises due to the loss of stability by one of the dipole transverse optical vibrations of the lattice in the paraelectric phase at low temperatures. When this mode ‘freezes’ at $T = T_c$, a dipole moment arises in every crystal cell. In the other group (order–disorder-type ferroelectrics), the dipole moments actually exist in the symmetric paraelectric phase; however, they are disordered at $T \geq T_c$. In Fig. 2, two typical samples of both ferroelectric

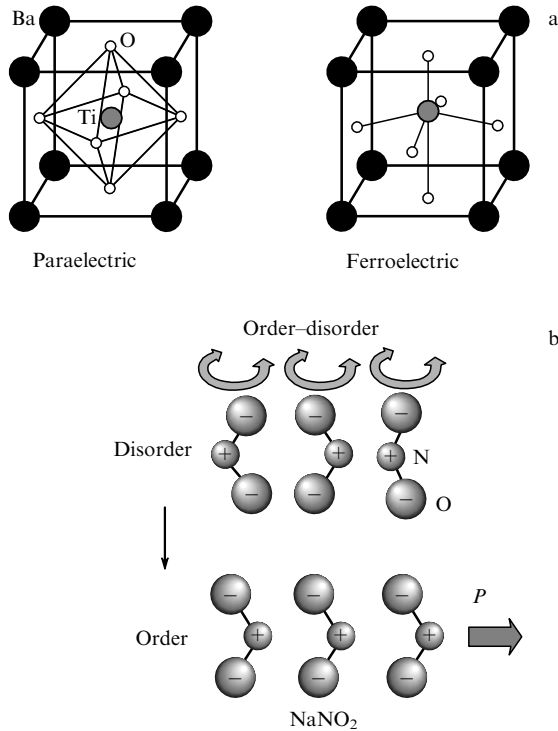


Figure 2. Structure of a ferroelectric before and after the phase transition: (a) a displacement-type ferroelectric BaTiO_3 with the Ti ion displaced along the (001) axis, (b) the order–disorder transition in NaNO_2 .

groups are shown. These are a perovskite BaTiO_3 crystal as an example of a displacement-type ferroelectric and an NaNO_2 crystal as an example of an order–disorder-type ferroelectric. In BaTiO_3 at $T = T_c$, a relative displacement of the Ti and O sublattices occurs, which is related to one of the transverse optical modes of perovskite oscillations. The transition in NaNO_2 is related to jumps of nitrogen ions and their ordering. In what follows, we do not deal with order–disorder-type ferroelectrics and only consider displacement-type transitions.

The relation between the microscopic theory of ferroelectric phase transitions in crystals and lattice dynamics was directly confirmed in experimental investigations of phonon spectra in displacement-type ferroelectrics. ‘Soft’ transverse optical (TO) lattice vibrations were observed in these crystals by means of infrared spectroscopy, Raman scattering, and inelastic scattering of thermal neutrons [5, 6]. It is obvious that the most important system properties responsible for the existence of the ferroelectric phase transition in crystals, namely, the instability of critical TO lattice vibrations at low temperature and the temperature dependence of the optical phonon frequency resulting in stabilized TO vibrations at high temperatures, can only be calculated in the framework of the microscopic theory of lattice dynamics. This is a rather difficult problem, which has not completely been solved yet.

In developing a consistent microscopic theory of the ferroelectric instability, simple models play an important role; in contrast to formal general expressions, simple models comprise information on qualitative features and distinctions in the crystal and electron structure and the type of chemical bonds for the compounds under study.

For a long time, in the framework of the simple atomic theory of ion crystals with the long-range Coulomb attraction between ions and short-range repulsion taken into account,

the approach to solving the ferroelectric instability problem was developed based on the idea of the contributions of short-range and long-range dipole forces (local field) to the squared frequency of the critical TO lattice vibrations (see review [2]).

All known ferroelectrics are dielectrics or semiconductors having greater or lesser bond ionicity. Hence, the simplest model capable of taking substantial features of the phenomenon into account is the model of polarizable point-like ions with charges Z_s^i and dipole electron polarizabilities of ions α_s (s is the sublattice index). In this model for a cubic crystal with two ions in an elementary cell [10], we can obtain the following expressions for the frequencies of the optical phonons with the momentum $q = 0$:

$$\Omega_{\text{TO}}^2 = \Omega_0^2 - \Omega_{\text{DD}}^2, \quad (2.14)$$

$$\Omega_{\text{LO}}^2 = \Omega_{\text{TO}}^2 + \frac{Z^2}{\epsilon_\infty} \Omega^2, \quad (2.15)$$

where $\Omega^2 = 4\pi e^2 / \mu v_0$, μ is the reduced mass of the cell, v_0 is its volume, Ω_0^2 is the positive contribution of short-range forces, and Ω_{DD}^2 is the negative contribution of the regular part of the dipole–dipole interaction (local field). An additional contribution to the frequency of longitudinal optical phonons Ω_{LO}^2 is associated with the macroscopic field arising under longitudinal optical (LO) vibrations of the lattice, which is responsible for the splitting of LO- and TO-frequencies in polar crystals.

It follows from (2.14) that the ferroelectric instability of the cubic phase arises under the condition $\Omega_0^2 < \Omega_{\text{DD}}^2$, which is possible due to either an anomalous reduction in Ω_0^2 or an anomalous increase in Ω_{DD}^2 . In a particular system, the choice between these two possibilities is hindered for a number of reasons. The main reason is the limited applicability of the model of polarized point-like ions for describing crystals with ferroelectric properties. The main problem in this model is the absence of a consistent microscopic description of the contribution of short-range forces to the optical frequencies, that is, of Ω_0^2 . However, it is possible to study the dependence of Ω_{DD}^2 on experimentally measured macroscopic parameters of an ion crystal in this model by writing the expression for Ω_{DD}^2 as

$$\Omega_{\text{DD}}^2 = (\epsilon_\infty + 2) \left(\frac{Z_i}{3} \right)^2 \Omega^2 = \frac{Z_{\text{eff}}^2}{\epsilon_\infty + 2} \Omega^2, \quad (2.16)$$

where $Z_{\text{eff}} = (\epsilon_\infty + 2)Z_i/3$ is the dynamic Born charge. The dielectric constant ϵ_∞ in this model is given by the known Lorentz–Lorenz formula

$$\epsilon_\infty = 1 + \frac{4\pi\beta/v_0}{1 - 4\pi\beta/(3v_0)}, \quad (2.17)$$

where $\beta = \sum \alpha_i$.

It follows from (2.14), (2.16), and (2.17) that an increase in the electron dielectric constant ϵ_∞ favors the greater contribution of the dipole forces to Ω_{DD}^2 , that is, a greater instability of TO vibrations of the lattice. An increase in the dynamic Born charge Z_{eff} should be simultaneously observed in this case. Just this behavior is observed in compounds with the structure like NaCl and CsCl. This tendency is more pronounced in semiconductor compounds A^4B^6 (GeTe, SnTe). Compounds A^4B^6 have a very small ‘ionicity,’ that is, their effective ion charges are very small: $Z_s \approx 0.2–0.3$. The contribution of dipole forces to Ω_{DD}^2 noticeably increases due to large permittivity values $\epsilon_\infty \approx 30–40$. It

can be shown [11] that the contribution of short-range forces, that is, the parameter Ω_0^2 , is not as small in A^4B^6 compounds as in other binary ion crystals and that the ferroelectric instability in these crystals is completely determined by the large contribution of the dipole–dipole interaction Ω_{DD}^2 .

In polyatomic cubic ferroelectrics with a perovskite-type structure, there is one more reason for the increased contribution of the dipole forces to Ω_{DD}^2 , which was first mentioned by Skanavi [12] and Slater [13]. This reason is related to the specific features of the local field factor f in polyatomic crystals, which determines the relation between the mean field \mathbf{E} and the local field \mathbf{E}_{loc} ($\mathbf{E}_{\text{loc}} = \mathbf{E} + f\mathbf{P}$). In two-atom crystals, the Lorentz factor of the local field is $f = 4\pi/3$. Calculation of internal fields in crystals with a perovskite-type structure performed in Refs [12, 13] shows that the internal field in the perovskite structure is not Lorentzian and some structural constants of the internal field are of the order of 30, that is, an order of magnitude greater than the Lorentz factor. This may result in an anomalously large contribution of dipole forces to one of the frequencies of TO lattice vibrations in the cubic phase.

The model approach to the ferroelectric instability problem given above and the conclusion concerning the role of the dipole–dipole forces and local field factors in the origin of ferroelectricity in ion crystals have often been criticized. This is mainly connected with the model treatment of the interaction forces in ion crystals. However, in the framework of the exact microscopic theory of lattice dynamics, Kvyatkovskii [14, 15] showed that relations (2.14) and (2.16) are valid not only for the model of the polarized atom but also for all types of ion crystals.

Before starting the discussion of microscopic theories of lattice dynamics and ferroelectric instability, we consider an important problem concerning the concept of polarization itself, which is a principal part in the theory of ferroelectricity. The above speculations were based on the classical consideration of ion crystal physics. This is not critical because the phenomenon of ferroelectricity, in contrast to magnetism, may exist in the framework of classical physics as well. It is known [16] that the macroscopic polarization \mathbf{P} for a finite-size body is the mean polarization density field $\mathbf{p}(\mathbf{r})$:

$$\mathbf{P}(\mathbf{r}) = \frac{1}{V} \int \mathbf{p}(\mathbf{r}) \, d\mathbf{r}, \quad (2.18)$$

where V is the body volume. According to the Maxwell equations, the polarization density $\mathbf{p}(\mathbf{r})$ satisfies the relation

$$\text{div } \mathbf{p}(\mathbf{r}) = -\rho(\mathbf{r}), \quad (2.19)$$

where $\rho(\mathbf{r})$ is the total charge density. The polarization $\mathbf{p}(\mathbf{r})$ exists only inside the body. Using Eqn (2.19) and integrating (2.19) by parts, we obtain

$$\mathbf{P}(\mathbf{r}) = \frac{1}{V} \int \mathbf{r} \rho(\mathbf{r}) \, d\mathbf{r} + \int_S \mathbf{r}(\mathbf{p}(\mathbf{r}) \, d\mathbf{S}). \quad (2.20)$$

We may choose the integration surface in (2.20) outside the body, in which case the second term in (2.20) vanishes. Thus, the macroscopic polarization of a finite-size sample is uniquely determined by its dipole moment, that is, by the first term in (2.20), which completely agrees with the statement presented at the beginning of this review.

It is not easy to define the concept of polarization for an electrically neutral system with a periodic charge density

distribution. The dipole moment of such a system depends on how the sample was cut, on its surface condition, and so on. Moreover, the absolute value of the polarization can be neither defined theoretically nor measured (see review [3] and the references therein). We can only measure the variation of polarization if some external factors change, such as the external electric field or the internal state of the crystal, for example, as a result of the phase transition from the nonpolar to the ferroelectric phase. Such variations are determined by the bulk properties of the crystal and this part of the polarization can be theoretically defined for an infinite sample as well. For this, we should consider the variation of polarization $\Delta\mathbf{P}$ rather than the polarization \mathbf{P} itself. It is convenient to separate the variation of polarization into a sum of two contributions, the contribution of the displacements of atomic nuclei and the electron contribution:

$$\Delta\mathbf{P} = \Delta\mathbf{P}_{\text{nucl}} + \Delta\mathbf{P}_{\text{el}}. \quad (2.21)$$

In the case of the ferroelectric transition, the contribution of atom nuclei is determined as [10]

$$\Delta\mathbf{P}_{\text{nucl}} = \frac{1}{v_0} \Delta\mathbf{d}_{\text{nucl}} = \frac{1}{v_0} \sum_s Z^{\text{nucl}}(s) \Delta\mathbf{R}(s), \quad (2.22)$$

where v_0 is the volume of the elementary cell and $Z^{\text{nucl}}(s)$ and $\Delta\mathbf{R}(s)$ are the charge and displacement of the s th nucleus. Summation in (2.22) ranges over a single elementary cell. Expression (2.22) represents the dipole moment resulting from ion displacements.

The electron contribution to the polarization can be determined as [17]

$$\Delta\mathbf{P}_{\text{el}} = \frac{1}{v_0} \int_{\Omega_0} \delta\mathbf{p}_{\text{el}}(\mathbf{r}) \, d\mathbf{r}, \quad (2.23)$$

where $\delta\mathbf{p}_{\text{el}}(\mathbf{r})$ satisfies an equation similar to Eqn (2.19):

$$\text{div } \delta\mathbf{p}_{\text{el}}(\mathbf{r}) = -\delta\rho(\mathbf{r}) \quad (2.24)$$

with $\delta\rho(\mathbf{r})$ being the electron density variation due to the displacement of nuclei. Integrating Eqn (2.23) by parts, we obtain the electron contribution to the polarization of the crystal in the form

$$\Delta\mathbf{P}_{\text{el}} = \frac{1}{v_0} \int_{\Omega_0} \mathbf{r} \delta\rho(\mathbf{r}) \, d\mathbf{r} + \frac{1}{v_0} \int_S \mathbf{r}(\mathbf{n} \delta\mathbf{p}_{\text{el}}) \, dS. \quad (2.25)$$

The first term in (2.25), in addition to nucleus displacement (2.22), yield the dipole moment of an elementary cell. However, there exists the additional term in (2.25), which actually describes the transfer of polarization between cells. In the case of polarizable point-like ions, this term is zero and the crystal polarization is given by the sum of the dipole moments of elementary cells. For a continuous electron charge distribution, as in crystals, we just do not know, as was mentioned in Ref. [17], how to proceed with the second summand in (2.25), especially if we calculate the uniform polarization of the crystal as a whole. Based on this fact, it was concluded in [17] that the density distribution in an elementary cell of a periodic crystal is not sufficient for determining its polarization. Moreover, it was stressed that each term in (2.25) depends on the choice of the elementary cell; however, their sum is invariant with respect to such a

choice. Hence, to exactly define the value of the electron contribution to the polarization, we need some additional information on the properties of the periodic distribution of density or should use some other definition of the polarization distinct from that defined by Maxwell equation (2.19). In the framework of classical physics, we can represent the variation in the electron density as

$$\delta\rho(\mathbf{r}) = \sum_n \delta\rho_n(\mathbf{r} - \mathbf{R}_n). \quad (2.26)$$

This means that the variation in the electron density is directly related to its variation in each ion. Then we can rewrite Eqn (2.19) for the Fourier components of the charge density and polarization in the form

$$i\mathbf{q} \delta\mathbf{p}(\mathbf{q}) = -\delta\rho(\mathbf{q}). \quad (2.27)$$

Now we obtain the following expression for the variation of the electron density in the long-range approximation ($\mathbf{q} \rightarrow 0$):

$$i\mathbf{q} \delta\mathbf{p}(\mathbf{q}) = \frac{1}{V} \int d\mathbf{r} \exp(i\mathbf{q}\mathbf{r}) \sum_n \delta\rho_n(\mathbf{r} - \mathbf{R}_n). \quad (2.28)$$

Expanding the exponential in a small vector \mathbf{q} , we obtain

$$i\mathbf{q} \delta\mathbf{p}(\mathbf{q}) = \frac{1}{V} \int d\mathbf{r} (1 + i\mathbf{q}\mathbf{r}) \sum_n \delta\rho_n(\mathbf{r} - \mathbf{R}_n). \quad (2.29)$$

Using the electric neutrality condition

$$\int d\mathbf{r} \delta\rho(\mathbf{r}) = 0, \quad (2.30)$$

we find

$$\delta\mathbf{P}(0) = \frac{1}{v_0} \sum_s \delta\mathbf{d}_s, \quad (2.31)$$

where $\delta\mathbf{d}_s$ is the dipole moment of the s th ion and the sum is taken over s within a single elementary cell:

$$\delta\mathbf{d}_s = \int \mathbf{r} \delta\rho(\mathbf{r}) d\mathbf{r}. \quad (2.32)$$

Thus, expression (2.31), in addition to the contribution of the displacements of nuclei in (2.22), does yield the dipole moment of an elementary cell in this model.

Even if we distract ourselves from the difficulties related to the definition of polarization, it is clear that any calculation of electron density variations, which inevitably arise in ferroelectric transitions, should be performed within quantum mechanics. Presently, the most popular quantum mechanical approach to the calculation of properties of an electron–ion system is the density functional method [18]. We consider such calculations in Section 3.

3. First-principle calculations of ferroelectric systems

We do not thoroughly consider the density functional method here, and only recall some important details. It has been proved that the energy of the ground state of a system of interacting particles (in our case, electrons) is a unique functional of the density distribution $\rho(\mathbf{r})$ for these particles,

and hence $\rho(\mathbf{r})$ implicitly defines all the properties of the ground state of the system. The actual density distribution is given by the minimum condition for the energy functional:

$$\frac{\delta E_{\text{el}}\{\rho(\mathbf{r})\}}{\delta\rho(\mathbf{r})} = 0. \quad (3.1)$$

The electron energy includes the kinetic energy, the energy of the interaction with ions, the Coulomb interaction between electrons, and the exchange–correlation energy. Nominally, it can be written in the form

$$E_{\text{el}} = E_{\text{kin}} + E_{i-e} + E_{e-e} + E_{\text{xc}}. \quad (3.2)$$

Kohn and Sham [19] suggested seeking a solution of Eqn (3.1) for the density $\rho(\mathbf{r})$ in the form of the density of a system of noninteracting electrons placed in an external self-consistent field:

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2. \quad (3.3)$$

For the wavefunctions $\psi_i(\mathbf{r})$, we can write the Kohn–Sham equation [19] as

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{eff}}(\mathbf{r}) \right) \psi_i = \varepsilon_i \psi_i, \quad (3.4)$$

where $V_{\text{eff}}(\mathbf{r})$ is the effective potential.

All the parameters needed for finding the total electron energy and the effective potential, except the exchange–correlation energy, are known. Within various approximations for the exchange–correlation energy (we do not consider them due to the limitations of our review; for further details, see reviews [20] and [21]), these equations can be solved and the total crystal energy for various crystal structures can be calculated. This approach also allows calculating the electron contribution to the dynamic matrix of crystal vibrations.

Since the 1980s, several ion crystal properties have been calculated [22–24], including the properties of oxides with a perovskite structure, by the density functional method. It was found from these calculations that the energy of the distorted ferroelectric phase in BaTiO₃, KNbO₃, and PbTiO₃ crystals is less than that of the cubic phase. In an SrTiO₃ crystal, the so-called antiferrodistortion phase has a minimal energy. In Fig. 3, the calculation results are shown [22] for the total energy of a BaTiO₃ crystal as a function of the Ti ion deviation u from the equilibrium. It follows that just the rhombohedral lattice is the most energetically preferable crystal structure at $T = 0$. Calculation results are also given for various volumes of an elementary cell, showing that at a smaller cell volume, i.e., at higher pressure, the energy difference between the paraelectric and ferroelectric phases reduces. This means that at a sufficiently small pressure, the phase transition to the ferroelectric state disappears. This fact additionally hinders first-principle calculations because it is difficult to precisely determine the equilibrium distances between atoms. In some works, the phonon spectra of perovskite crystals in the cubic phase were also calculated. It was shown that at $T = 0$, these spectra have an unstable optically active mode with $\omega_{\text{TO}}^2(\mathbf{q}) \leq 0$.

Despite good success in calculating eigenenergies for various phases of ion crystals, it is difficult to distinguish a physical reason for a particular instability of the cubic phase.

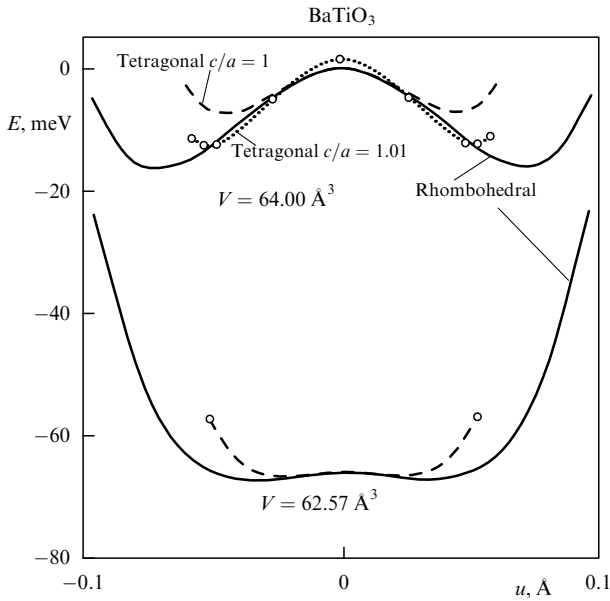


Figure 3. Calculation of rhombohedral (solid line) and tetragonal (dashed line) phase energies at various ratios of the lattice parameter c/a for two volumes of an elementary cell.

Nevertheless, as was shown above, the nature of the ferroelectric instability has been determined in the framework of phenomenological theories of ion crystals. It is explained by a large negative-sign contribution from polar-active phonon modes of long-range dipole–dipole interactions between ions. The concepts of ions and ion dipoles are absent in the framework of the density functional method and we are only dealing with a periodic distribution of the charge density, which is given by sum (3.3) over Bloch wave functions. Moreover, the serious problems mentioned above inevitably arise in this approach in describing the electric polarization of an ion crystal with a periodic electron density distribution.

In the early 1990s, an approach was suggested for determining the uniform polarization of a periodic crystal [25, 26], which avoided the difficulties concerning determination of the dipole moment in the theory of infinite systems. This approach is based on the definition of polarization in terms of the current across the system:

$$\frac{\partial \mathbf{P}_{\text{el}}(\mathbf{r})}{\partial t} = \mathbf{j}_{\text{el}}(\mathbf{r}, t). \quad (3.5)$$

Relation (3.5) can be easily verified by using (2.24) and the continuity equation

$$\text{div } \mathbf{j}_{\text{el}}(\mathbf{r}, t) + \frac{\partial \rho_{\text{el}}(\mathbf{r}, t)}{\partial t} = 0. \quad (3.6)$$

Writing (3.5) in terms of Fourier components $\mathbf{P}_{\text{el}}(\mathbf{q}, \omega)$ and $\mathbf{j}_{\text{el}}(\mathbf{q}, \omega)$, we obtain

$$\mathbf{P}_{\text{el}}(\mathbf{q}, \omega) = -i \frac{\mathbf{j}_{\text{el}}(\mathbf{q}, \omega)}{\omega}. \quad (3.7)$$

In the adiabatic approximation $\omega \rightarrow 0$, the expression for the static and uniform polarization takes the form

$$\mathbf{P}_{\text{el}} = - \lim_{\omega \rightarrow 0} \left(\lim_{\mathbf{q} \rightarrow 0} \text{Im} \frac{\mathbf{j}_{\text{el}}(\mathbf{q}, \omega)}{\omega} \right). \quad (3.8)$$

The current operator, in contrast to the coordinate operator, is a well-defined parameter and its mean value over the quantum mechanical state of the system can also be easily calculated in the case of a crystal with periodic boundary conditions. Finally, under a variation of the external parameter λ (for example, a displacement of the ion sublattice), the electron polarization is given by the formula

$$P_x^\lambda = \frac{2e}{(2\pi)^3} \text{Im} \sum_{n=1}^M \int d^3k \left\langle u_{\mathbf{kn}}^\lambda \left| \frac{\partial}{\partial k_x} \right| u_{\mathbf{kn}}^\lambda \right\rangle, \quad (3.9)$$

where $u_{\mathbf{kn}}(\mathbf{r})$ is the Bloch amplitude periodic in \mathbf{r} , n is the zone index, and the sum is taken over filled zones. The integral in the right-hand side of Eqn (3.9) is closely related to the so-called Berry phase [27] for the n th zone. We consider neither the relation between the Berry phase and the electron polarization nor the technique for calculating the crystal polarization by using this approach. These problems are thoroughly considered in recent review [28].

All the problems mentioned above concerning the use of the density functional method for ion crystals led some investigators to conclude [28, 29] that all classical theories of ion crystals are wrong. The reasons are as follows. In the framework of this approach, it is impossible to introduce the concept of well-defined ions in a crystal, and hence the concept of crystal polarization as a sum of dipole moments of individual ions has no physical meaning. Based on formulas (3.5)–(3.9), the authors of [28, 29] reached the conclusion that the crystal polarization is determined by the current across the crystal and is expressed in terms of the Berry phase of Bloch periodic functions rather than in terms of a redistribution of the electron charge and variation of the dipole moment of the cell. We note that the use of the Berry phase for describing a polarization process in crystals is not a transition to new physics but merely the use of another mathematical language.

Kvyatkovskii [30] showed that Eqn (3.9) for the electron polarization can be obtained in the framework of the long-wavelength approximation by using the dipole moment operator instead of the current operator. We do not discuss the details of this work. We only note that formula (3.9) directly entails the conclusion needed. With this aim, we use the known relation [30]

$$(u_{\mathbf{nk}}^\lambda | r | u_{\mathbf{mk}}^\lambda) = i \left(u_{\mathbf{nk}}^\lambda \left| \frac{\partial}{\partial k} \right| u_{\mathbf{mk}}^\lambda \right). \quad (3.10)$$

Integration over the coordinate in (3.10) is taken within a single elementary cell; hence, the integral in the left-hand side of (3.10) has a well-defined value. From formulas (3.9) and (3.10), we can also conclude that under changing the parameter λ , the polarization varies due to either a current flow or a change in the dipole moment of the elementary cell.

This circumstance is more pronounced in another approach to the calculation of ion crystal properties, which has been developed by our group at the Theoretical Department of the Lebedev Physical Institute, Russian Academy of Sciences [31–36]. This approach, which we call the method of the deformable and polarizable ion, is based on representing the total electron density in a crystal in the form of a sum of individual densities of overlapping ions rather than as the density of a system of noninteracting electrons residing in a self-consistent periodic potential. We note that this approach, similarly to the Kohn–Sham method, is based on the density

functional method and is therefore a first-principle approach. We briefly describe the essence of the method in Section 4. It is thoroughly considered in our papers [30–36], in review [3], and in works by a group from Krasnoyarsk, which successfully used this method for calculating various properties of ion crystals (see, e.g., Refs [37–39]).

4. The method of the deformable and polarizable ion

The total electron density in a crystal can be represented as a sum of individual densities of overlapping ions:

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r} - \mathbf{R}_i). \quad (4.1)$$

The total crystal energy can then be written as

$$E^{\text{cr}} = E \left\{ \sum_i \rho_i(\mathbf{r} - \mathbf{R}_i) \right\} + E^{\text{N}}, \quad (4.2)$$

where E^{N} is the energy of interacting nuclei (or ions),

$$E^{\text{N}} = \frac{e^2}{2} \sum_{i,j} \frac{Z_i^{\text{N}} Z_j^{\text{N}}}{|\mathbf{R}_i - \mathbf{R}_j|}, \quad (4.3)$$

Z_i^{N} is the nucleus charge, and the electron contribution to the total energy is given by formula (3.2). This approach was used by Jensen and Lenz [40, 41] in the early 1930s. For the kinetic and exchange-correlation energies, they used the local approximation suggested by Thomas [42] and Fermi [43]. The density functional method involving expression (4.1) for the electron density was used for calculating properties of ion crystals by Kim and Gordon [44]. The electron density $\rho_i(\mathbf{r} - \mathbf{R}_i)$ for an individual ion was calculated in that work by the Hartree–Fock method. It was assumed in [44] that during the formation of a crystal, the electron density distribution in each particular ion remains constant in accordance with the ‘rigid’ ion model. For better convergence of the calculation, the sum of single ion energies can be added to and subtracted from the expression for the total energy:

$$E^{\text{cr}} = \left[E \left\{ \sum_i \rho_i(\mathbf{r} - \mathbf{R}_i) \right\} - \sum_i E \{ \rho_i(\mathbf{r} - \mathbf{R}_i) \} \right] + \sum_i E \{ \rho_i(\mathbf{r} - \mathbf{R}_i) \} + E^{\text{N}}. \quad (4.4)$$

By neglecting the overlapping of more than two ions simultaneously and the eigenenergy of ions added in (4.4) (the third summand), we can rewrite the expression for the total energy in the form

$$E^{\text{cr}} = \frac{e^2}{2} \sum_{i,j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_{i,j} V_{ij}, \quad (4.5)$$

where V_{ij} describes the short-range repulsion between ions and Z_i is the ion charge. Here, $Z_i = Z_i^{\text{N}} + Z_i^{\text{el}}$, and $Z_i^{\text{el}} = \int \rho_i(r) dr$. Thus, the Gordon–Kim model in its original form reduces in accordance with formula (4.5) to the known model of rigid ions [45]. The results of calculations in [44] show that this model with no adjustable parameters describes the static properties of alkali halide crystals sufficiently well. However, like any rigid ion model, it has some drawbacks because it does not account for the difference in the electron

density distributions for a free ion and for an ion residing inside a crystal. In addition, the Gordon–Kim model cannot be used for calculating some ionic crystals, in particular, peroxides, because the oxygen ion O^{2-} does not exist in the vacuum and is only stabilized in the crystal environment field. Moreover, in calculating ionic crystals, the possibility of the formation of a dipole and other multipole moments must be taken into account.

In solving these problems [46–48], a number of difficulties arose, which have not been overcome. One such problem is to determine the eigenenergy of an ion having multipole moments. It was shown above that in order to pass from expression (4.2) for the total crystal energy to formula (4.5), which has the form of the total energy in the rigid ion model, we had to subtract and add the sum of energies of single ions. In the Gordon–Kim approach, which uses the electron densities of free ions, the added sum of ion energies can be neglected because it is independent of the crystal environment.

The situation is quite different if multipole moments of ions are taken into consideration. In that case, we must specify what should be added to crystal energy (4.2) and subtracted from it if the electron density depends on these moments. This problem can be solved consistently only by using the methods developed by M A Leontovich in the theory of nonequilibrium thermodynamics [49], which was done in our work [31–36].

The essence of our generalizations of the Gordon–Kim model is as follows. First, according to the Leontovich nonequilibrium thermodynamics theory [49], we define a nonequilibrium state of each ion, in which the electron density distribution has a different multipole symmetry. This implies that we define ions having some effective radius K_0 , dipole moment \mathbf{P} , quadrupole moment \mathbf{Q} , and so on. For this, the Kohn–Sham equation is solved for a single ion with the auxiliary fields having the corresponding symmetries, which can be written as

$$V_{\text{ext}}(\mathbf{r}, K_l) = -r^l K_l P_l(\cos \theta), \quad (4.6)$$

where $P_l(\cos \theta)$ is the Legendre polynomial and, in the case of the dipole symmetry, K_l is just the amplitude of the external electric field. Solving the Kohn–Sham equation, we obtain the electron density distribution

$$\rho(\mathbf{r}) = \rho_0(K_0, \mathbf{r}) + K_l \delta \rho_l(K_0, \mathbf{r}) P_l(\cos \theta). \quad (4.7)$$

According to the standard electrostatics, we can define the multipole moment P_l as

$$P_l = K_l \int d\mathbf{r} r^l \delta \rho_l(K_0, \mathbf{r}) P_l(\cos \theta) \quad (4.8)$$

and the corresponding polarizability as

$$\alpha_l = \frac{P_l}{K_l} = \int d\mathbf{r} r^l \delta \rho_l(K_0, \mathbf{r}) P_l(\cos \theta). \quad (4.9)$$

Using the Leontovich nonequilibrium thermodynamic theory, we can calculate the eigenenergy of the ion and represent it in the form

$$E_{\text{ion}}^{\text{self}} = \int d\mathbf{r} \frac{Z\rho(\mathbf{r})}{|\mathbf{r}|} + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + F\{\rho(\mathbf{r})\}, \quad (4.10)$$

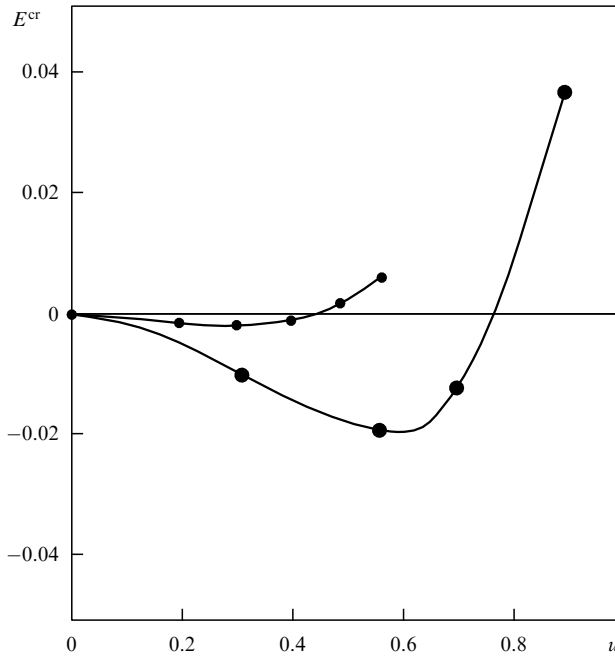


Figure 4. The energy of a BaTiO₃ crystal versus the ion displacement amplitude in the ferroelectric phase (zero energy is calculated from the cubic phase energy, the values on the axes are in atomic units). The large and small circles respectively refer to the results of calculations with quadrupole distortions of the oxygen ion density neglected and taken into account.

where $F\{\rho(\mathbf{r})\}$ is the contribution of the kinetic and exchange-correlation energies. Thus, the expression for the total energy can be written as

$$E^{\text{cr}} = \left[E \left\{ \sum_i \rho_i(\mathbf{r} - \mathbf{R}_i) \right\} - \sum_i E_{\text{ion}}^{\text{self}} \{ \rho_i(\mathbf{r} - \mathbf{R}_i) \} \right] + E^{\text{N}} + \sum_i E_{\text{ion}}^{\text{self}} \{ \rho_i(\mathbf{r} - \mathbf{R}_i) \}. \quad (4.11)$$

The nonequilibrium thermodynamic theory substantially simplifies the expression for the eigenenergy of an ion. In particular, the dipole contribution $E_{\text{ion}}^{\text{self}}$ can be reduced [36] to the simple expression known in classical electrostatics:

$$E_{\text{ion}}^{\text{self}} = \frac{P_l^2}{2\alpha_l}. \quad (4.12)$$

Just this value should be added to the expression for total energy (4.11).

We do not thoroughly discuss the results of our study performed in the framework of the model of deformable and polarizable ions; we just present some important examples. We have shown [35] that in the distorted ferroelectric phase in a BaTiO₃ crystal, the ion displacements from the equilibrium state of the cubic phase agree well with experimental data only if both dipole and quadrupole distortions of the electron density for oxygen ions are taken into account. If only the dipole distortions are taken into account, then the ion displacements are overestimated by a factor of two and the reduction in the total energy in the ferroelectric phase is overestimated by an order of magnitude, as shown in Fig. 4. In simple models for the polarizable ion, this circumstance was ignored.

Another example is the calculation of the electron contribution to the dielectric constant ϵ_∞ . We have shown that if only the dipole distortions of the electron density are taken into account, the expression for the total energy formally coincides with that obtained in the most general phenomenological model of deformable and polarizable ions. In our approach, all the parameters involved in the formula for the total energy are explicit density functionals, in contrast to the case in phenomenological models, and can be calculated by numerical methods relatively easily. With a term that describes the interaction of the dipole with the electric field added to the total energy, we can calculate the dipole moment from the minimum energy condition. Solving the equation for \mathbf{P} thus obtained and recalling that

$$\epsilon_\infty = 1 + \frac{4\pi P}{E}, \quad (4.13)$$

we obtain

$$\epsilon_\infty = 1 + \frac{4\pi\alpha_c^{(1)}}{1 - (4\pi/3)\alpha_c^{(1)}}, \quad (4.14)$$

where α_c is the polarizability of the elementary cell. We note that we obtained an expression of the Clausius–Mossotti type for the dielectric constant of a crystal, which is a direct consequence of the long-range dipole–dipole interactions between elementary cells. The cell polarizability obtained in our approach substantially differs from the sum of polarizabilities of free ions. It comprises the effects of both the non-Lorentzian corrections for a local field and the short-range dipole–dipole interactions. We showed earlier [3] that these differences can be substantial.

We can also obtain an analytic expression for the dynamic Born charge Z_{eff} [12], which describes the origin of polarization in a crystal resulting from the shift of ion sublattices responsible for the transverse optical mode with the momentum $q = 0$. The expressions for Z_{eff} obtained in this way formally coincide with those in the most general phenomenological model of polarizable and deformable ions.

All this proves that our method of the deformable and polarizable ion can be substantially considered a microscopic justification of old (however, not necessarily wrong) phenomenological models. In addition, the method preserves the simplicity and clarity of the previous theories of ion crystals. Similarly to ‘old’ phenomenological theories, it illustrates the role of non-Lorentzian corrections for a local field in the phenomenon of electric polarization in perovskite crystals. In the framework of this approach, the problem of the ferroelectric instability becomes absolutely clear. This instability is caused by the dipole–dipole interaction between ions in an optically active mode. Our calculations also demonstrate the important role played by quadrupole distortions of the electron density of oxygen in the phenomenon of ferroelectric instability: these distortions promote stabilization of the soft optical mode, since without the quadrupole moment of oxygen, many perovskite crystals would be pyroelectrics rather than ferroelectrics. In addition, the correctness of the phenomenological models for an ion crystal in describing the nature of the ferroelectric transition confirmed by us in the framework of the density functional allows using such models in solving certain problems that are still being discussed in the theory of ferroelectricity.

One such problem is the nature of the ferroelectric transition, namely, the question of whether it is a displacement-type transition or an order–disorder transition. In the above consideration, we assumed that ferroelectric transitions in perovskite crystals are classic examples of the displacement-type transition. However, the nature of the ferroelectric transition in perovskites has been discussed for a long time.

5. Anomalies of X-ray diffused scattering in perovskites

The first discussion of possible transitions of the order–disorder type in perovskites has started since works by Homes et al. [50, 51], in which specific features of diffuse X-ray scattering observed in the cubic phase of BaTiO₃ and KNbO₃ crystals were reported. The intensity of the diffuse scattering had the shape of leaves in planes normal to the principal axes of the cubic crystal. These two-dimensional leaves disappeared systematically under phase transitions into tetragonal, orthorhombic, and rhombohedral structures.

For describing this phenomenon, the so-called eight-node model for the perovskite structure in the cubic phase was suggested [50, 51]. It is assumed in this model that already in the cubic phase, the center of equilibrium of an atom *B* resides not at the center of the cube formed by atoms *A* but at eight points on the four axes of the (1, 1, 1) type shown in Fig. 5. In the paraelectric phase, *B* atoms in different cells are statistically distributed over the eight nodes, which maintains the average cubic symmetry over the crystal. The eight-node model assumes that successive structural transformations in perovskites are transitions of the order–disorder type with the corresponding ordering of atoms in these eight cells over the whole crystal. We note that the absolutely random distribution of static displacements of *B* atoms over the eight cells does not result in the diffuse scattering observed. The authors of Refs [50, 51] assumed partial ordering of *B* atoms, which results in the occurrence of relatively long chains of such atoms in the directions (1, 1, 1). No physical reasons for this ordering were mentioned in Refs [50, 51].

Soon after paper [50] appeared, Hüller suggested an explanation of the specific diffuse scattering of X-rays observed in BaTiO₃ in the framework of the standard model of a ‘soft’ mode responsible for the displacement-type phase transition. The main idea is the possible existence of a strong

anisotropy for the soft optical transverse phonon mode in perovskite crystals. This mode is twice degenerate at $q = 0$ and its energy is actually constant for all wavevectors \mathbf{q} that reside in the (0, 0, 1) plane, with atom displacements parallel to the (0, 0, 1) axis. In other directions, the energy sharply increases as \mathbf{q} increases. This means that there are quasi-one-dimensional phonons in perovskite crystals. We note that an anisotropy of the soft mode arises, according to the analysis by Hüller [52], due to specific features of long-range Coulomb interactions, which, in turn, are related to the perovskite crystal structure and the presence of *B*–O–*B*–O... chains. Only these two modes were used by Hüller in the calculation of diffuse scattering.

In addition to the diffuse scattering in the cubic phase of perovskites, other specific physical properties were observed in some works, in particular, in the absorption of X-ray radiation (extended X-ray absorption fine structure, EXAFS) and in nuclear magnetic resonance (NMR) spectra. The results obtained in these works were interpreted as a confirmation of static displacements of the *B* atom from the central position already in the cubic phase. Recent measurements [53] of diffuse X-ray scattering in a PbTiO₃ compound did not reveal anomalies similar to those obtained in BaTiO₃ and KNbO₃. From this fact, the authors concluded that the soft modes cannot be the reason for the anomalies in the diffuse scattering of X-rays, because they exist in PbTiO₃ as well as in BaTiO₃ and KNbO₃.

Among the observed effects that were treated as a manifestation of the order–disorder-type transition, many phenomena are described by the same pair correlation function of displacements $M_{lk,l'k'}^{z\beta}(t)$, which can be written as [54]

$$M_{lk,l'k'}^{z\beta}(t) = \langle u_z(\mathbf{r}(lk), 0) u_\beta(\mathbf{r}(l'k'), t) \rangle, \quad (5.1)$$

where $u_z(\mathbf{r}(lk), t)$ is the time-dependent component of the atom displacement in a crystal in the direction α from the equilibrium position at the point $\mathbf{r}(lk)$, l is the cell number, and k is the position of the atom in the cell. The mean value denoted by the angular brackets should be taken over the Gibbs ensemble for dynamic atom vibrations and over various configurations in the case of a disordered crystal.

In calculating diffuse scattering, Hüller writes the energy of relevant modes in the form

$$\omega_{1,2}^2(\mathbf{q}) = \omega_0^2(T) + A_{1,2} \left(\frac{\mathbf{q}}{|\mathbf{q}|} \right) \mathbf{q}^2. \quad (5.2)$$

According to Hüller’s idea, all anharmonic effects are included in $\omega_0(T)$ and it is the only parameter dependent on the temperature. The dispersion of the considered soft mode is determined by the dipole–dipole interaction of ions and by their electron polarization. In this case, the coefficient $A_{1,2}(\mathbf{q}/|\mathbf{q}|)$ differs by a factor of 30 for various \mathbf{q} vector directions due to the local field effects mentioned above.

A correct description, in particular, of the temperature dependence of diffuse scattering, requires that contributions of all phonon modes rather than of the soft mode only be taken into account. With this aim, we recently thoroughly calculated [55] the phonon spectra for the cubic phase of BaTiO₃, KNbO₃, and PbTiO₃ compounds by using the phenomenological model of polarizable shells. This model was first used by Cawley [56] for calculating the phonon spectra of the perovskite SrTiO₃ crystal. Later, it was often

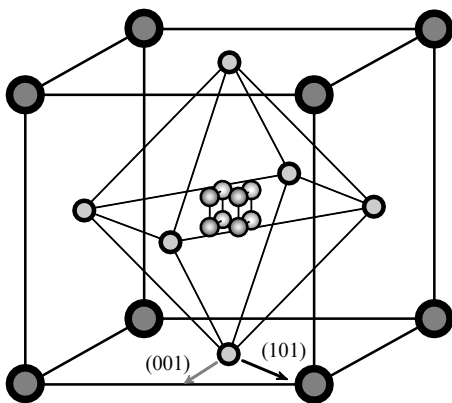


Figure 5. Perovskite structure in the eight-node model (the equilibrium positions of a *B* ion are shown by eight points near the center of the cube).

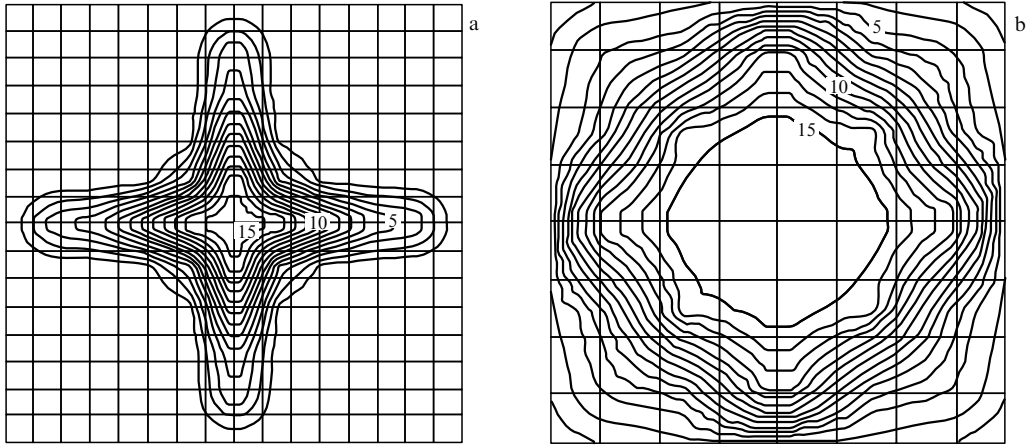


Figure 6. Pair correlation function $B(\mathbf{r})$ for the pairs Ti–Ti (a) and Ba–Ba (b) in BaTiO₃. Nodes of the coordinate grid correspond to the positions of Ti (a) and Ba (b) atoms. Numbers give the values of $B(\mathbf{r})$.

used in calculations of numerous characteristics of perovskites and other ion crystals, in particular, for calculating the temperature dependence of phonon spectra. This model was thoroughly considered in our work [55], where references to previous works are presented. We have calculated phonon crystal spectra and one-time pair correlation functions of displacements for BaTiO₃, KNbO₃, and PbTiO₃.

Our calculations of phonon spectra show that the dispersion of the soft optical mode in KNbO₃ bears a strong resemblance to that in the Hüller model. We note that there is a good agreement of the calculated phonon spectra at $T = 0$ with the results of first-principle calculations in [57]. The phonon spectra agree well not only in the high-symmetry directions but also in the whole Brillouin zone. This means that our calculations involve unstable transverse optical modes for all the wavevectors \mathbf{q} in the plane normal to the (001) axis, and the polarization vectors of these modes are directed along the (100) axis. Actually, these modes are responsible for one-dimensional vibrations of ions in Ti–O–Ti–O– chains. The situation is similar with BaTiO₃. It is quite different in the case of PbTiO₃, where the optical mode does not have the anisotropy as strong as in KNbO₃ and BaTiO₃, and quasi-one-dimensional phonons are absent. This fact is explained by the participation of lead in ion displacements in the soft optical mode, which is confirmed by eigenvector calculations for this mode. This means that the chain structure B–O–B–O– and the corresponding specific features of the Coulomb dipole–dipole interaction are not revealed in the dynamics of the PbTiO₃ lattice. This fact is mainly related to the high polarizability of the Pb ion. It is shown below that such behavior of the soft optical mode, in particular, affects the diffuse scattering of X-rays.

We have also calculated the phonon spectra in the cubic phase for perovskites at $T \geq T_c$. Stabilization of the soft optical mode in the framework of our model was performed by reducing the polarizability of the oxygen ion. Contour height plots are given in Fig. 6 for the scalar function $B(\mathbf{r}(lk))$ related to the pair correlation function $M_{lk, l'k'}^{z\beta}(t)$ as

$$B(\mathbf{r}(lk)) = \frac{1}{r^2(lk)} \sum_{\alpha, \beta} r_{\alpha}(lk) M_{lk}^{z\beta} r_{\beta}(lk) \quad (5.3)$$

for Ti–Ti and Ba–Ba pairs in a BaTiO₃ compound. A difference in the functions $B(\mathbf{r}(lk))$ for Ti–Ti and Ba–Ba pairs can be seen in the figure. The function for the Ti–Ti pair is actually diagonal in Cartesian coordinates ($\approx \delta_{x\beta}$) and exhibits a long-distance correlation. In this respect, it is similar to the function obtained by Hüller [52] in the calculation with only the soft mode taken into account. The function $B(\mathbf{r}(lk))$ for barium ions has no peculiarities and is standard, as in systems with a quasi-isotropic phonon spectrum. In PbTiO₃, the function $B(\mathbf{r})$ for all ion pairs has no explicit maxima along the axes and exhibits an almost spherically symmetric dip at the origin, similarly to the case of a Ba–Ba pair in BaTiO₃. Such behavior of the functions is related to the properties of the phonon spectra for the compounds under consideration or, to be more precise, to the properties of the polarization vectors of soft modes. In BaTiO₃, there actually exist quasi-one-dimensional phonons connected with the vibrations of titanium and oxygen ions in the chains Ti–O–Ti–O–. In PbTiO₃, lead ions are directly involved in the soft mode and there are no quasi-one-dimensional phonons.

Next, we briefly consider the diffuse scattering in BaTiO₃, in which the scattering on barium and oxygen ions can be neglected because of the small scattering on these ions compared to that on titanium ions. In this case, we can write the expression for the scattering intensity as

$$S(\mathbf{q}) = N \exp(-2M(\mathbf{q})) \sum_{l,k} \exp[-i\mathbf{q}\mathbf{r}(lk)] M_{lk}^{z\beta} q_{\alpha} q_{\beta}, \quad (5.4)$$

where $\mathbf{r}(l)$ are the distances between Ti ions.

Our calculations show that if, in contrast to only the soft mode in the Hüller model, all phonon modes are taken into account, then the pair correlation function can be represented in the form

$$M_l^{z\beta} = f(\mathbf{r}(l)) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (5.5)$$

under the constraint $\mathbf{r}(l) = (0, 0, na)$, where a is the distance between neighboring Ti ions. This function can be represented similarly for $\mathbf{r}(l) = (0, na, 0)$ and $\mathbf{r}(l) = (na, 0, 0)$. Such a coordinate dependence of $M_l^{z\beta}$ results in the occurrence of three independent sums in the intensity along the

crystallographic axes of the type

$$N \exp(-2M(q_x)) \sum_n \exp(-iq_x n a) M(na) q_x^2. \quad (5.6)$$

It follows from (5.6) that for all vectors of the reciprocal lattice $q_x = 2\pi n/a$, there is a maximum independent of the vector components q_y and q_z . This means that there are planes normal to the x axis in the intensity of the diffuse scattering. The scattering planes normal to the y and z axes arise similarly. Thus, the appearance of diffuse X-ray scattering in BaTiO₃, KNbO₃, and PbTiO₃ crystals can be easily explained without invoking the eight-node model or additional static ordering of atoms. The results of EXAFS and NMR experiments can also be explained in the framework of the dynamic approach with an anisotropic soft mode. A detailed discussion of these problems is far beyond the scope of this review.

6. Conclusion

We briefly summarize our discussion concerning the evolution of theoretical concepts of the nature of the ferroelectric transition in ion crystals. First, we note that already in the framework of the phenomenological theory of ferroelectricity, V L Ginzburg formulated the concept of the soft mode whose frequency tends to zero as the temperature becomes close to the phase transition temperature. Experimentally and then theoretically, it was shown that the soft mode is an optically active transverse phonon mode with the momentum $q = 0$.

In the framework of the simplest lattice dynamics models, it was shown that a soft mode arises from the competition of two contributions to the dynamic vibration matrix: the short-range repulsion between ions and the long-range dipole-dipole attraction.

Further development of first-principle methods for calculating the physical properties of crystals in the framework of the density functional theory (DFT) allowed calculating the energies of cubic and ferroelectric phases and showing that the energy of the ferroelectric phases is more beneficial compared to the paraelectric cubic phase. In the present report, we have shown that in the DFT framework with the electron wavefunctions represented as the sum of Bloch functions, interpretation of the reason for the ferroelectric transition and determination of the nature of crystal polarization are problematic. There are also contradictions with the results obtained earlier in the framework of simple phenomenological models for ion crystals. It was also shown that the first-principle method for the polarizable and deformable ion developed in our works, first, allows thoroughly calculating the properties of ion crystals and, second, may appreciably substantiate old phenomenological theories. Differences in the interpretation of the results in the two approaches are mainly connected with different mathematical methods used rather than with physical results.

In this report, we disregard problems of consistently taking the anharmonicity effects into account. In particular, in discussing the specific features of diffuse X-ray scattering, we calculated the dynamics of perovskite crystals in the quasi-harmonic approximation, which neglects the attenuation of phonon excitations. We have shown in [55] that the attenuation effects can hardly change the results on the nature of anomalous diffuse X-ray scattering. The fact is that exactly anisotropic quasi-one-dimensional phonons are strongly

damped, and hence the attenuation is also anisotropic. This means that in calculating the pair correlation function of displacements, we should use the exact spectral density of the single-particle Green's function. Because the displacement function is expressed by an integral over the whole spectrum, the anisotropy of this function is also preserved. The results can only slightly qualitatively change.

In addition to the attenuation of soft modes near the phase transition into a ferroelectric state, a central line of inelastic scattering arises, whose nature is still unclear. A systematic anharmonic theory of lattice dynamics for ferroelectric crystals is necessary for describing all these effects. This problem has not been solved yet. There are also a number of other unsolved problems in the theory of ferroelectricity, so we have much interesting work before us.

I am sincerely grateful to V L Ginzburg for his persistent support of my work in the physics of ferroelectricity and to L V Keldysh and O E Kvyatkovskii for the numerous useful discussions.

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