Physics of the Solid State, 2025, Vol. 67, No. 2

06

Electrostatic mechanism of ferroelectric instability

© *P.I. Arseev*

Lebedev Physical Institute, Russian Academy of Sciences,
Moscow, Russia

E-mail: ars@lpi.ru

Received December 1, 2024
Revised January 26, 2025
Accepted January 28, 2025

A microscopic mechanism of ferroelectric instability is proposed, based on the idea that in the ferroelectric phase, the main state of the system should be a state with a nonzero constant electric field inside the crystal. It is shown that this approach can provide a unified description of the physical mechanism for transitions that have traditionally been considered transitions of different types: „displacement type“ and the „order-disorder“ type. The dependence of free energy on polarization differs from the Ginzburg–Landau functional, although it has similar properties and is reduced to the usual Ginzburg–Landau functional near the transition temperature.

Keywords: Ferroelectric phase transition.

DOI: 10.61011/PSS.2025.02.60682.327

1. Introduction

Historically, ferroelectricity has been considered as a phenomenon almost completely analogous to ferromagnetism. This analogy led to the fact that the concept of local electric polarization (electric dipoles) was the basis of the theory. The occurrence of macroscopic polarization was interpreted as the alignment of existing (or emerging) electric dipoles in a crystal in one direction [1–3]. Therefore, the order parameter has traditionally been associated with some kind of lattice distortion or atomic displacement. The theory was based on the Ginzburg–Landau (GL) functional [4], in which the order parameter was called the polarization of the system, understood as a certain quantity associated with the displacement of the atoms of the crystal.

At the same time, there was an understanding of the fact that it is not possible to introduce the concept of local static electric polarization in a crystal from the point of view of electrodynamics because of the ambiguity of its definition, unlike the phenomenon of magnetism. There have been attempts to correct the situation by considering not the polarization as such, but the changes of polarization in case of the ferroelectric transition. For example, R.Resta formulated the so-called „modern theory of ferroelectricity“, which considered the change of polarization and currents flowing through the crystal at the moment of switching to the ferroelectric state [5,6]. These quite correct arguments, however, did not provide an answer about the physical mechanism of the occurrence of the macroscopic field. The current understanding of ferroelectric physics is described, for example, in Ref. [7] and a brief overview in Ref. [8].

If we associate the occurrence of polarization with structural distortions of the lattice, then we have to answer the question why in some cases the structural transition is accompanied by the occurrence of ferroelectricity, and in some cases not. It seems more logical to directly use the average field inside the crystal (i. e., polarization in the direct electrodynamic sense) as an order parameter.

We are discussing here only proper ferroelectrics, the order parameter of which is represented by a vector quantity. To explain and describe the mechanisms of improper ferroelectric phase transitions with order parameters of a more complex structure, it is necessary to construct a more complex description (see chapter 4 in Ref. [3]).

This article proposes a new view on the cause of the ferroelectric state, based on the idea that the main feature of ferroelectric is that it is a material for which it is „beneficial“ to be in a state with a certain constant electric field in volume. In this sense, the specific mechanism of providing this field with charges at the edges of the ferroelectric becomes secondary. But the main question is under what conditions the occurrence of a constant electric field inside the sample is energetically beneficial.

It is possible to imagine the situation as the occurrence of instability in such a complete system: a ferroelectric sample in between plates with a charge transfer between them. A charge spontaneously occurs on the plates due to instability. In another language, this instability can be interpreted as the occurrence of a divergence in the dielectric permittivity. The relation of the acquired expressions with the experimental situation is discussed in more detail in Section 5.

The proposed approach does not contradict the GL theory, which is phenomenological in nature and always valid near the transition temperature. However, in our approach, we try to answer the question of the microscopic causes of the transition, and this allows expanding the GL theory beyond taking into account only the first terms of the free energy expansion in the Taylor series with respect to polarization. It can also be noted that the modern theory of ferroelectricity complements the approach presented here by describing the currents that will appear inside the sample when charge is transferred from one edge of the sample to the other in order for a constant field to appear in the sample.

Describing the macroscopic details of ferroelectric behavior, the physics associated with the division into domains, etc., is an independent task. A coherent picture of many phenomena has developed in this field over the decades. However, it seems that a new look at microscopic instability may lead to a new understanding of a number of macroscopic phenomena.

2. Instability mechanism

Using the example of two classical ferroelectrics $NaNO_2$ and $BaTiO_3$, we will try to show that the division of ferroelectrics into different types, conventionally called „order-disorder“ and „displacement“ [9], is not necessary and these ferroelectrics can be described qualitatively in exactly the same way.

To begin with, let's consider a more obvious example of a ferroelectric $NaNO_2$, in which the transition is classified as „order-disorder“. $NaNO_2$ has a group of atoms NO_2, which can occupy two equivalent positions in the lattice (Figure 1).

From the point of view of microscopy, the system is equivalent to the quantum problem of states in a two-well potential. The position of the system in the minimum of one of the wells corresponds to the state when two oxygen atoms are turned „down“, while they are turned „up“ in the other well.

Then the Hamiltonian of the system in the space of these two states has the form:

$$H = \begin{bmatrix} \varepsilon_0 & V \\ V & \varepsilon_0 \end{bmatrix}. \tag{1}$$

Here V is the tunnel matrix element of the transition between these two states. If an electric field appears in the system, then the energy positions of the group of atoms „down“ and „up“ become unequal because this group of atoms has a nonzero dipole moment (see Figure 2). The Hamiltonian of interaction with a field E:

$$H_{int} = \begin{bmatrix} Ed & 0 \\ 0 & -Ed \end{bmatrix}, \tag{2}$$

where d is the dipole moment of this group of atoms.

The change of energy of the ground state in case of an occurrence of a constant field is given for Hamiltonians (1), (2) by the usual formula for two bound states

$$\Delta\varepsilon = (V - \sqrt{V^2 + (Ed)^2}). \tag{3}$$

The change of the total free energy of the entire system — sample plus the electric field per lattice cell is equal to:

$$\Delta F = \Delta\varepsilon + \frac{1}{8\pi} E^2 v_0, \tag{4}$$

where v_0 is the volume of the unit cell.

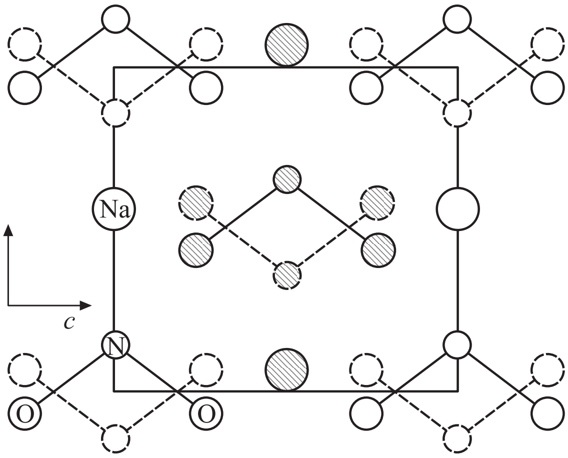

Figure 1. Lattice $NaNO_2$. The group of atoms NO_2 can occupy two equivalent positions.

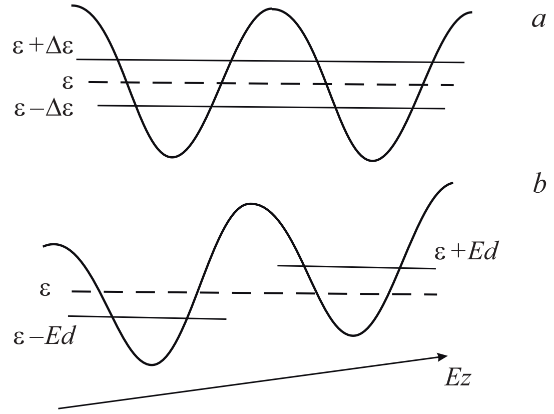

Figure 2. a — quantum states of the group NO_2 as states of a particle in a two-well potential; b — changes of levels when an electric field occurs due to the dipole moment of the group NO_2.

The free energy depends on the magnitude of the field as a parameter. The equilibrium value of the field is determined by the minimum of the function:

$$\Delta F(E) = \left[V - \sqrt{V^2 + (Ed)^2}\right] + \frac{1}{8\pi} E^2 v_0. \tag{5}$$

This function has the following form in dimensionless variables:

$$\Delta F(P) = V\left[1 - \sqrt{1 + P^2} + \kappa P^2\right], \tag{6}$$

where P is the dimensionless macroscopic polarization of the system

$$P = (Ed)/V,$$

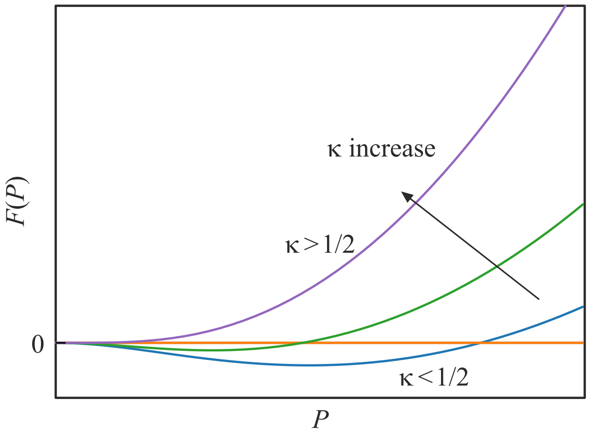

Figure 3. Change of the dependency of the function $F(P)$ in case of change of the parameter κ.

and the position of the minimum of the function (6) is defined by a single dimensionless parameter κ:

$$\kappa = \frac{V v_0}{8\pi d^2}. \tag{7}$$

The graph of this function for different values κ is shown in Figure 3.

With values of

$$\kappa < \frac{1}{2}, \tag{8}$$

there is a minimum at $P \neq 0$. In this case, it is beneficial for the system to switch to a state with a nonzero electric field in the volume. This is the ferroelectric transition within the framework of our approach, which corresponds from the point of view of electrodynamics to the divergence of the dielectric permittivity of the symmetric praphase to infinity.

These arguments are similar to the usual Ginzburg–Landau (GL) approach, except that the free energy functional of the order parameter P (6) does not have the form of an ordinary power functional of GL. It is shown below that the GL functional of the usual form is obviously restored near the transition temperature, where the order parameter is small.

3. Temperature of transition

What happens with an increase of temperature can be seen in a standard way by calculating the partition function Z and the free energy $F(T, E) = -T \ln Z$.

For the simple case of an effective description of the essential ferroelectric states $NaNO_2$ by the Hamiltonian (1), (2):

$$F(T, E) = \left[\varepsilon_0 - \sqrt{V^2 + (Ed)^2}\right] - T \ln\left[1 + e^{-\frac{2\sqrt{V^2 + (Ed)^2}}{T}}\right] + \frac{v_0}{8\pi} E^2. \tag{9}$$

Or in the given variables:

$$\Delta F(T, E)/V = (F(T, E) - F(T, 0))/V$$

$$= [1 - \sqrt{1 + P^2} + \kappa P^2] - \tau \ln\left[\frac{1 + e^{-\frac{\sqrt{1+P^2}}{\tau}}}{1 + e^{-\frac{1}{\tau}}}\right], \tag{10}$$

where the dimensionless temperature $\tau = T/2V$.

The change of the dependence of $F(P)$ on temperature is shown in Figure 4.

The equilibrium value of the field at a given temperature will be determined from the condition

$$\frac{\partial F(T, E)}{\partial E} = 0 \quad \text{or} \quad \frac{\partial F(\tau, P)}{\partial P} = 0, \tag{11}$$

which leads to an equation on $P(T)(E(T))$ of the form

$$2\kappa = \frac{1}{\sqrt{1 + P^2}} \tanh\left[\frac{\sqrt{1 + P^2}}{2\tau}\right]. \tag{12}$$

This equation is equivalent to the necessary condition (8) for the occurrence of polarization for $T = 0$. As the temperature increases, the second multiplier in (12) always decreases as $1/\tau$ and, starting from some τ_c, only the trivial minimum $E = 0$ remains.

The critical temperature τ_c corresponds to the disappearance of P, that is, it is determined from the condition

$$2\kappa = \tanh \frac{1}{2\tau_c}. \tag{13}$$

Except for the case when κ is close to $1/2$, this condition provides a qualitative assessment

$$\tau_c \simeq 1/4\kappa \quad \text{or} \quad T_c \simeq \frac{4\pi d^2}{v_0}, \tag{14}$$

and at the same time, the condition (8) should be fulfilled.

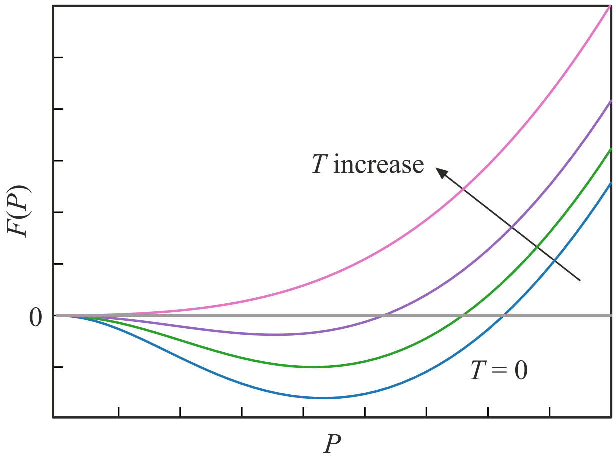

Figure 4. Changes $F(P)$ with the increase of the temperature.

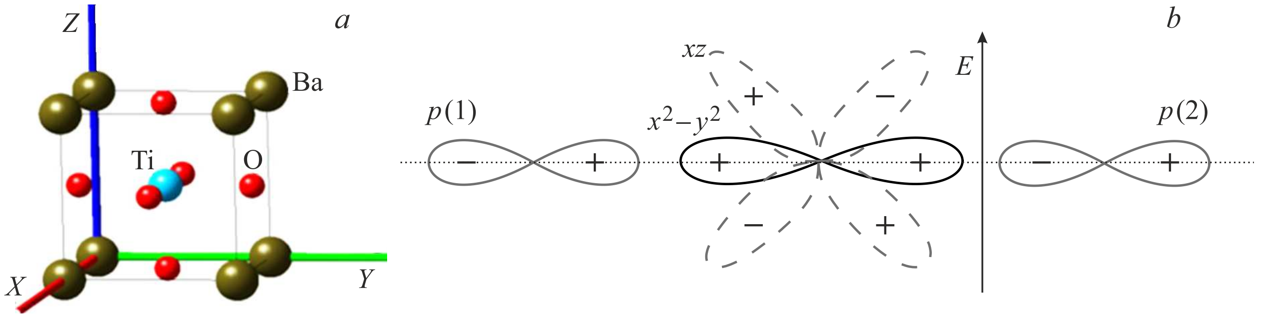

Figure 5. *a* — lattice cell BaTiO$_3$; *b* — simplified description of the ferroelectric transition mechanism in BaTiO$_3$. Only two p_x orbitals of oxygen atoms closest to titanium and $d_{x^2-y^2}$, d_{xz} orbitals of titanium are considered.

When taking into account other quantum levels, the estimated T_c will not change qualitatively: if the distance to other levels is greater than T_c, their role will be exponentially suppressed. The estimate changes by a numerical factor of the order of 1 at similar levels, like probably in compounds of type BaTiO$_3$.

The GL functional of the usual form can be restored from (10) near T_c, when the dimensionless polarization of P is small:

$$\Delta F(T,P)/V = a(\tau)P^2 + b(\tau_c)P^4, \qquad (15)$$

where the coefficients have the form:

$$a(\tau) = \frac{1}{2\tau_c^2}\,\frac{1}{ch^2(1/\tau_c)}\,(\tau - \tau_c),$$

$$b = \frac{1-2\kappa}{8\tau_c}\left[\tau_c + \frac{1}{ch^2(1/2\tau_c)}\right]. \qquad (16)$$

As it should be, the coefficient a becomes negative below T_c, while coefficient $b > 0$ at $\kappa < 1/2$ (8).

4. Barium titanate

Let's show that for barium titanate, the mechanism of ferroelectric instability can be described qualitatively in a very similar way to the previous case, despite the fact that this transition has historically been called a transition of „displacement" type. It was believed that during the ferroelectric transition, the titanium atoms shift, that is, the dipole moment changes, which causes the polarization.

Here we will focus only on the first (from the side of high temperatures) phase transition from a symmetrical cubic phase to a tetragonal one. The full picture of the transitions in BTO is quite complex; three phase transitions with a change of structure are observed in this compound. The other two transitions below the temperature are significantly related to structural changes in the lattice, and other mechanisms need to be discussed for them. All four phases of barium titanate have been extensively studied numerically, starting with one of the first papers [10]. Hybrid approaches are currently used to study transitions between different phases, in which molecular dynamic calculations are performed using potentials acquired from first principles calculations [11,12]. Such calculations make it possible to visualize the atomic displacements characteristic of certain changes in the lattice structure and confirm the existence of four phases in the BTO. However, in our opinion, neither these calculations nor the numerical results indicating the instability of the lattice associated with „soft modes" fully explain the initial physical causes of these instabilities.

Some displacement of atoms obviously takes place during the transition, but it is not the primary reason for the occurrence of polarization within the framework of the considered approach.

The structure of the lattice cell BaTiO$_3$ is shown in Figure 5, *a*. The levels t_{2g} (d_{xy}, d_{xz}, d_{zy}) of titanium in the octahedral environment are lower than e_g $(d_{x^2-y^2}, d_{z^2})$. Two orbitals e_g hybridize with three p-orbitals of surrounding oxygens directed at the titanium atom and form 5 zones near the Fermi level. The orbitals t_{2g} each hybridize with two pairs of corresponding p-orbitals of oxygens directed „orthogonally" towards titan. (Figure 5, *b* shows one such pair for the orbital d_{xz} — these will be the orbitals p_z on the nearest oxy along the axis X, and the second pair comprises orbitals p_x on the nearest axes Z). There are three more identical groups of 3 zones. Since these 9 zones change only slightly when a constant field is applied, in a simplified picture to grasp the essence, we will refer to the level d_{xz} rather than the „generated" zones.

For the set of states shown in Figure 5, *b*, the states d_{xz} in the cubic praphase do not hybridize with neighboring oxygen states p_x by symmetry. However, the situation changes if an electric field is applied along the z axis.

In this picture, the main mechanism of the occurrence of ferroelectricity is the occurrence of hybridization between pairs of states d_{xz}, p_x and d_{yz}, p_y in the presence of an electric field along the axis z, which leads to a decrease of the energy of the lower levels occupied by electrons.

The eigenenergies of the simplified cluster model are determined from the following determinant:

$$\begin{vmatrix} \varepsilon_p-\varepsilon & 0 & t & p \\ 0 & \varepsilon_p-\varepsilon & -t & p \\ t & -t & \varepsilon_d-\varepsilon & 0 \\ p & p & 0 & \varepsilon_t-\varepsilon \end{vmatrix} = 0, \qquad (17)$$

(column order: $p_x(1), p_x(2), d_{x^2-y^2}, d_{xz}$). The oxygen levels ε_p are the deepest, the levels ε_t of the orbitals t_{2g} lie below the levels ε_d of the orbitals e_g: $\varepsilon_p < \varepsilon_t < \varepsilon_d$. The matrix element of the transition t describes the hybridization of orbitals forming states near the Fermi level in a crystal:

$$t = \langle d_{x^2-y^2} | V_{at} | p_x \rangle.$$

The energy levels

$$\varepsilon_{1,2} = \frac{1}{2}\left[\varepsilon_d + \varepsilon_p \pm \sqrt{(\varepsilon_d-\varepsilon_p)^2 + 8t^2}\right]$$

determine the energy of these hybridized Ti and O states from which the valence band and conduction band are formed in the crystal.

When the field is applied, the states d_{zx} and p_x hybridize, and their hybridization is described by the dipole moment matrix element over z between these states.

$$p = eE\langle d_{xz}|z|p_x\rangle \equiv eEd_z.$$

The energy levels are now determined by the equation:

$$(\varepsilon-\varepsilon_1)(\varepsilon-\varepsilon_2)\left[(\varepsilon_t-\varepsilon)(\varepsilon_p-\varepsilon) - 2p^2\right] = 0.$$

When the field $(p \neq 0)$ is applied, the oxygen level ε_p decreases by

$$\Delta_p = \frac{1}{2}\left[\sqrt{(\varepsilon_t-\varepsilon_p)^2 + 8p^2} - (\varepsilon_t-\varepsilon_p)\right], \qquad (18)$$

and the level $d_{xz}$of titanium increases by the same value. Our simplified model describes only „half“ of states, since there are still exactly the same states along the axis Y. Therefore, the occupation of states in this model should correspond to 1 electron on d_{xz} orbital of titanium, and 4 electrons on 2 p-shells of oxygen. The ground state without a field has energy:

$$W_0 = 2\varepsilon_2 + 2\varepsilon_p + \varepsilon_t,$$

and when the field appears, it becomes:

$$W_E = 2\varepsilon_2 + 2(\varepsilon_p - \Delta_p) + (\varepsilon_t + \Delta_p) = W_0 - \Delta_p. \qquad (19)$$

The energy gain is doubled when taking into account the states along the axis y:

$$\Delta F(E) = -2\Delta_p(E) + \frac{1}{8\pi}E^2 v_0. \qquad (20)$$

Taking into account the explicit form Δ_p (18), we obtain an expression of the same form (6) in dimensionless variables as for sodium nitrite

$$\Delta F(E) = V\left[1 - \sqrt{1+P^2} + \kappa P^2\right], \qquad (21)$$

only the dimensionless polarization and coefficients are equal here:

$$P = \frac{2\sqrt{2}p}{(\varepsilon_t-\varepsilon_p)}, \quad V = (\varepsilon_t-\varepsilon_p),$$

$$\kappa = \frac{(\varepsilon_t-\varepsilon_p)v_0}{64\pi(ed_z)^2}. \qquad (22)$$

There is a minimum of free energy at $E \neq 0$ just as for $NaNO_2$ if the condition (8) is fulfilled: $\kappa < 1/2$.

If such a transition from the cubic praphase to the state with $E \neq 0$ takes place, then, of course, there is some deformation of the lattice and a slight displacement of the Ti atoms stabilizing this structure. But in the considered approach, the displacements and deformation of the lattice play an auxiliary, „subsidiary“ role, they are rather an indicator of the transition, but not the cause of the appearance of polarization for the first transition of the „proper ferroelectric“ type. It seems more logical that the field itself — that is, polarization in the literal sense of the word — should become an order parameter instead of atomic displacements, which are present in any structural transition that is not accompanied by the appearance of ferroelectricity. A number of numerical calculations of the stability of various BTO structures also show that the displacement of, for example, titanium atoms during the first transition is very small [13].

In the language of the band structure, the mechanism of instability of the cubic praphase remains qualitatively the same, but instead of talking about filling of the levels of the cluster under consideration, we should talk about filling of bands, some of which shift in the presence of a constant field along the direction Z. Let's briefly show what happens in the band language. There are 2 groups of bands near the Fermi level: 5 bands originating from the hybridization of orbitals $d_{x^2-y^2}$ and d_{z^2} with 3 p-orbitals of neighboring oxygen atoms directed at the titanium atom, and 3 groups of three bands originating from hybridization of the same structure each of the three t_{2g} states with four p-orbitals of neighbors corresponding to symmetry. (The band structure of barium titanate was calculated in more detail, for example, in Refs. [14,15]). The main features of these bands are easily reproduced in the tight-binding approach. Thus, the dispersion relations of the first five bands associated with e_g-orbitals are determined by the following determinant ($k_{x,y,z}$ — components of a dimensionless wave vector lying in the range $[-\frac{\pi}{2}, \frac{\pi}{2}]$):

$$\begin{vmatrix} \varepsilon_p - \varepsilon & 0 & 2it\sin k_x & 0 & 2i\,\dfrac{t}{\sqrt{3}}\sin k_x \\ 0 & \varepsilon_p - \varepsilon & 2it\sin k_y & 0 & -2i\,\dfrac{t}{\sqrt{3}}\sin k_y \\ -2it\sin k_x & -2it\sin k_y & \varepsilon_d - \varepsilon & 0 & 0 \\ 0 & 0 & 0 & \varepsilon_p - \varepsilon & 4i\,\dfrac{t}{\sqrt{3}}\sin k_z \\ 2i\,\dfrac{t}{\sqrt{3}}\sin k_x & 2i\,\dfrac{t}{\sqrt{3}}\sin k_y & 0 & -4i\,\dfrac{t}{\sqrt{3}}\sin k_z & \varepsilon_d - \varepsilon \end{vmatrix} = 0 \qquad (23)$$

(column order: p_x, p_y, $d_{x^2-y^2}$, p_z, d_{z^2}). There are following relations for matrix elements of hybridization in the case of cubic symmetry:
if

$$t = \langle d_{x^2-y^2}|V_{at}|p_x\rangle,$$

then

$$\langle d_{z^2}|V_{at}|p_x\rangle = \frac{t}{\sqrt{3}}, \quad \langle d_{z^2}|V_{at}|p_z\rangle = 2\,\frac{t}{\sqrt{3}}.$$

There is one dispersion-free band in the spectrum $E_p = \varepsilon_p$ and 4 bands with dispersion, which are easily found from equation (23). For instance, we have two more bands without dispersion $E_1 = \varepsilon_p$, $E_2 = \varepsilon_d$ and 2 bands with the following spectrum in the direction $\Gamma - X$ in the Brillouin zone ($k_y = k_z = 0$):

$$E_{3,4}(k_x) = \left(\frac{\varepsilon_p + \varepsilon_d}{2}\right) \mp \sqrt{\left(\frac{\varepsilon_p - \varepsilon_d}{2}\right)^2 + \frac{16}{3}t^2\sin^2 k_x}. \qquad (24)$$

Similarly, it is possible to find a spectrum of 9 states originating from orbitals d_{xz}, d_{yz} and d_{xy}. These are three identical spectra in three bands, the laws of dispersion of which are determined by the same determinant as the upper-left block 3×3 (23) with the replacement $\varepsilon_d \to \varepsilon_t$ and another matrix element of overlap t'. Schematically, these bands near Γ — points are shown in Figure 6.

When an electric field appears along the axis Z, as was the case in the simple model, there is also a hybridization of states d_{zx} with p_x along the axis X and d_{zy} with p_y along the axis Y, described by the matrix element of the dipole moment along z between these states.

$$p = eE\langle d_{xz}|z|p_x\rangle = eE\langle d_{yz}|z|p_y\rangle.$$

Then, in the general determinant defining the spectrum, the elements $2p\cos k_x$ and $2p\cos k_y$ appear, connecting the lower bands from the group „e_g“ of bands with 2 (out of three) „t_{2g}“ bands extending from the point ε_t. Due to this coupling, the initial bands are split as shown in Figure 6 with a dotted line.

We would like to remind that, starting from the formula (17), the energy levels are indicated as follows: ε_p — the atomic oxygen level, ε_d — the level of $d_{x^2-y^2}, d_{z^2}$ titanium and ε_t — the level of d_{xz}, d_{yz}, d_{xy} titanium.

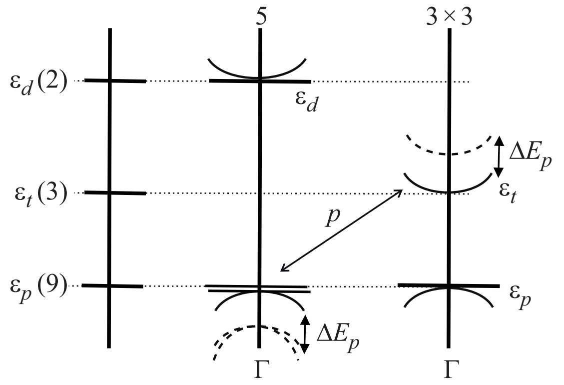

Figure 6. Diagram of the formation of bands from the initial atomic levels of titanium and oxygen at the point Γ. The degree of degeneracy of each atomic level (excluding spin) is shown in parentheses. The hybridization of orbitals leads to the appearance of 5 bands of states e_g and 3 identical groups of 3 bands of states t_{2g}. These bands are shown separately. Two bands are split off along Z down from the level ε_p and up from the level ε_t when the field (P) is applied. The amount of splitting at point Γ is given by the formula (25).

Since the lower bands are completely filled, and the upper ones are empty, the displacement of the bands down from the level ε_p always leads to a decrease of the total energy of the band electrons. The exact answer for this decrease can only be acquired by summing over all states of the Brillouin zone, since the decrease in band energy is different for different k, however, the situation is very simple at point Γ (see (23) and (24) for $k = 0$). Without the field, the energies of the bands at point Γ are simply ε_p, ε_d and ε_t, and the hybridization resulting from the field displaces 2 bands from the lower group e_g of bands down and two bands from the upper group t_{2g} of bands up. The magnitude of this displacement is:

$$\Delta E(p) = -\left(\frac{\varepsilon_t - \varepsilon_p}{2}\right) + \sqrt{\left(\frac{\varepsilon_t - \varepsilon_p}{2}\right)^2 + (2p)^2}. \qquad (25)$$

Taking into account the electron spin, the estimate of the decrease in energy by the displacement of the bands at the point Γ yields:

$$\Delta W = W_E - W_0 \simeq 4\Delta E(p). \tag{26}$$

We see that (25) is an expression of the same type as (18) in the cluster model.

Thus, in both the simplified cluster model and the band picture for barium titanate, the main mechanism of ferroelectricity is the appearance of hybridization between pairs of states d_{xz}, p_x and d_{yz}, p_y in the presence of an electric field along the axis z. This hybridization leads to a decrease of the energy of the lower filled bands, which turns out to be beneficial for the system.

We see that in the case of the „order-disorder" transition, and in the case of „displacement" type transitions (formulas (5), (20)) the dependence of free energy on the field, as on the order parameter, has the same qualitative form in dimensionless variables, shown in Figure 3, and this dependence ((6), (21)) differs from the usual GL. (Of course, such a literal coincidence occurs only in simplified models).

5. Role of the external electric field

Let's discuss how the described instability can manifest itself from the point of view of a real experimental situation. The situation where a ferroelectric sample is located between two metal plates connected by a wire was actually described above. At the same time, the energy of the entire system in the „state of the ferroelectric praphase and the plate without charge" turned out to be greater than the energy of the „ferroelectric phase of the sample and the nonzero charge on the plates". It is most convenient to extend this ideology to the situation with a given voltage on the plates as follows. Let us imagine that an external capacitor of very high capacity C_0 with a given charge Q is connected in parallel with the experimental capacitor in which the sample is located. Then the change of the charge due to the flow to the „experimental" capacitor small charge δQ corresponds to the change of the energy of the large capacitor by

$$(Q - \delta Q)^2/2C_0 \simeq -\delta Q(Q/C_0) = -\delta Q U_{\text{ext}}.$$

This energy should be added to the formulas ((5), (21)). It can be assumed that the variable on which the free energy of the entire system depends is the change of the charge on the plates of the „working" capacitor δQ. The field (polarization) E that appeared before is the field created by this change of the charge:

$$E = 4\pi \delta Q/S, \tag{27}$$

where S is the area of the plates. We will use the former designation E (and the dimensionless one P), understanding its relation to alternating charge (27). Now the formulas ((5), (21)) have the following form:

$$\Delta F(P) = V\left[1 - \sqrt{1 + P^2} + \kappa P^2 + P P_{\text{ext}}\right], \tag{28}$$

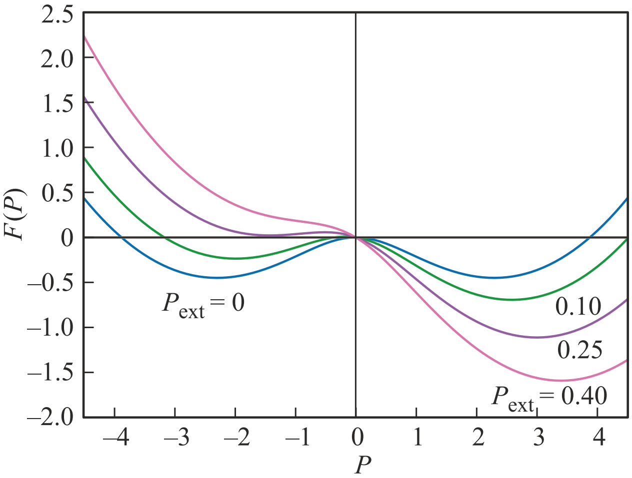

Figure 7. The change of the dependence $F(P)$ when an external voltage is applied. Parameter $\kappa = 0.2$. The values of the external voltage (arbitrary units) used in the formula (29) for each curve are shown in the figure.

where P_{ext} is a given dimensionless value of the external potential fixed by an external large capacitor. In initial values

$$P_{\text{ext}} = \frac{a^3}{4\pi d}\frac{U_{\text{ext}}}{L}, \tag{29}$$

where L is the thickness of the sample.

Figure 7 shows how the dependence of the free energy on the parameter P changes with a change of the external potential.

If the ferroelectric was in one of two stable minimum positions with polarization in a certain direction, the external voltage adding charge in the same direction does not significantly change the equilibrium value of the field. However, when the external voltage tends to change the charge on the „working" capacitor to the opposite, then the minimum disappears with an increase of the external voltage, instability occurs and the ferroelectric switches to another stable state with polarization in the opposite direction. If we draw the position of the minima in Figure 7 as a function of the external voltage, we get the hysteresis loop shown in Figure 8, which is given in all textbooks and reviews on ferroelectrics, and exactly corresponds to the classical experimental measurements according to the Sawyer-Tower scheme [7,16].

A current pulse passes at the moment of „polarization switching", transferring charges on the „working" capacitor from one plate to another, if the voltage on this capacitor is applied by an external source. This effect is also a well-established experimental fact.

The presence of a charge on an external capacitor or ions adsorbed from the environment on the surface of a ferroelectric is essential for explaining many macroscopic properties, details of polarization switching processes, limits of stability of states in a particular system, etc. These

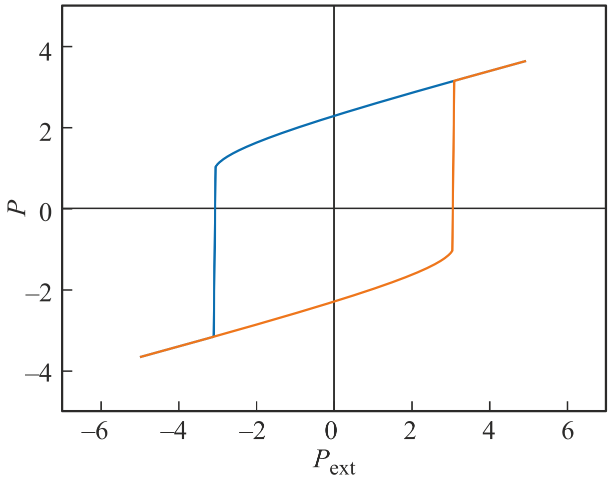

Figure 8. Hysteresis based on the dependence of polarization on external voltage. Parameter $\kappa = 0.2$.

phenomena were discussed in detail in a recent review in Ref. [17].

6. Concluding remarks

Whether a symmetric praphase will transition to a ferroelectric state depends on the value of the parameter κ (8). The formula (7) can be written as follows in the case of sodium nitrite:

$$\kappa = \frac{1}{8\pi\alpha^2}\frac{V}{V_{at}}, \tag{30}$$

where the volume of the lattice cell $v_0 = a_0^3$ (a_0 is the lattice constant) was taken, the characteristic energy of the Coulomb potential $V_{at} = e^2/a_0$, and the dipole moment of the group NO_2 is expressed in units of the dipole moment ea_0: $d = \alpha e a_0$. Apparently, we need to consider $\alpha \leq 0.1$. In its meaning, the value V is related to the energies characteristic of ion motion in a crystal, and V_{at} are characteristic electronic energies. Then $V \simeq (10^{-2}\text{–}10^{-3})V_{at}$. Taking $\alpha = 2\cdot 10^{-2}$, we obtain $\kappa \simeq 10^2\frac{V}{V_{at}} \simeq 1\text{–}0.1$, the criterion can be fulfilled. Then the transition temperature $T_c \simeq 10^{-2}V_{at}$, which roughly corresponds to the known T_c at a reasonable value $V_{at} \simeq 4\,\text{eV}$.

Similarly, for barium titanate (22):

$$\kappa = \frac{1}{64\pi\alpha^2}\frac{(\varepsilon_t - \varepsilon_p)}{V_{at}}, \tag{31}$$

here, the dipole moment d_z is written as $d_z = \alpha e a_0$. From the known data $\frac{(\varepsilon_t-\varepsilon_p)}{V_{at}} \leq 1$, then the ferroelectric transition criterion can be fulfilled at $\alpha \simeq 0.1$.

These estimates cannot claim to be absolutely accurate, however, they show that agreement with the experiment can be achieved with reasonable values of the parameters. There are no obvious physical limitations for the parameter κ (30), (31) that lead to the requirement $\kappa \gg 1$ or $\kappa \ll 1$. (For example, if the dipole moment d_z between neighboring atoms was required to be greater than the characteristic intraatomic moment ea_0, this would be unrealistic). This leads to the fact that a small quantitative difference of the parameters of even similar compounds can ensure the appearance or absence of ferroelectricity, which is observed experimentally.

7. Conclusion

Thus, it is shown for the first time that to describe the mechanism of ferroelectric instability for a class of intrinsic ferroelectrics, there may be a single approach for transitions that have traditionally been considered transitions of different types. The approach is based on the study of the behavior of the free energy of the total system — crystal plus electric field. In this case, it is the proper field that becomes the parameter of the order of the theory. The appearance of a minimum of free energy at a finite value of the field order parameter means the appearance of ferroelectricity, which in another language corresponds to the divergence of the dielectric permittivity of the praphase to infinity. The free energy functional of a symmetric praphase at zero temperature has the form ((6), (21)) and differs from the classical GL in that the equilibrium value of the order parameter (fields E) may be outside the range of applicability of only the first terms of Taylor series expansion of the free energy in powers of E near $E = 0$, as in the usual GL functional. Only at temperatures close to T_c does the expantion of the free energy (10) into the Taylor series lead to the usual form of the functional GL.

Funding

This work was funded by the Institute's budget. No additional grants have been received to conduct or manage this particular study.

Conflict of interest

The author declares that he has no conflict of interest.

References

[1] G.A. Smolensky, V.A. Bokov, V.A. Isupov, N.N. Kraynik, R.E. Pasynkov, M.S. Shur. Segnetoelektriki i antisegnetoelektriki. Nauka, M. (1971) p. 476. (in Russian).
[2] V.G. Vaks. Vvedenie v mikroskopicheskuyu teoriyu segnetoelektrichestva. Nauka, M. (1973) p. 328. (in Russian).
[3] B.A. Strukov, A.P. Levanyuk. Fizicheskie ocnovy cetnetoelektricheskikh yavleniy v kristallakh. Nauka, M. (1983) p. 240. (in Russian).
[4] L.D. Landau, E.M. Lifshitz. Elektrodinamika sploshnykh sred. Gl. 2. Nauka, M. (1982) p. 621. (in Russian).
[5] R. Resta. Ferroelectrics **136**, 51 (1992).
[6] R. Resta. Rev. Mod. Phys. **66**, 899 (1994).
[7] K. Rabe, Ch.H. Ahn, J.-M. Triscone (Eds.) Physics of ferroelectrics, Topics in applied Physics **105**. Springer, Berlin Heidelberg (2007).

[8] A.P. Levanyuk, B.A. Strukov. Encyclopedia of Condensed Matter Physics, ch. Ferroelectricity, 192–201, Elsevier (2005).
[9] G.A. Smolensky, N.N. Krainik. Sov. Phys. Usp. **97**, 657 (1969). (in Russian).
[10] W. Zong, D. Vanderbilt, K.M. Rabe. Phys. Rev. Lett. **73**, 1861 (1994).
[11] Jingtong Zhang, L. Bastogne, Xu He, Gang Tang, Ya-jun Zhang, P. Ghosez, Jie Wang. Phys. Rev. B **108**, 134117 (2023).
[12] L. Gigli, M. Veit, M. Kotiuga, G. Pizzi, N. Marzari, M. Ceriotti. Nature: npj computational materials **8**, 209 (2022).
[13] R.A. Evarestov, A.V. Bandura. J. Comput. Chem. **33**, 1123 (2012).
[14] S. Saha, T.P. Sinha, Abhijit Mookerjee. Phys. Rev. B **62**, 8828 (2000).
[15] D. Bagayoko, G.L. Zhao, J.D. Fan, J.T. Wang. J. Phys.: Condens. Matter **10**, 5645 (1998).
[16] M. Dawber, I. Farnan, J.F. Scott. Am. J. Phys. **71**, 819 (2003).
[17] S.V. Kalinin, Y. Kim, D.D. Fong, A.N. Morosovska. Rep. Prog. Phys. **81**, 036502 (2018).

Translated by A.Akhtyamov