

## PROGRESS IN FERROELECTRICITY\*

G. A. SMOLENSKIĬ and N. N. KRAÏNIK

Semiconductor Institute, U.S.S.R. Academy of Sciences, Leningrad

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## 1. INTRODUCTION

ALMOST 25 years have elapsed since the discovery and investigation of the ferroelectric properties of barium titanate by M. M. Vul.<sup>[1]</sup> It was precisely this discovery which provided the impetus for the development of the physics of ferroelectricity, now an independent branch of solid state physics.

The investigations of V. L. Ginzburg,<sup>[2-5]</sup> Anderson,<sup>[6]</sup> and Cochran<sup>[7]</sup> laid the groundwork for the dynamic theory of ferroelectricity, in which the problem of ferroelectricity is connected with the general dynamic theory of the crystal lattice.<sup>[8]</sup> It is important to emphasize that the analysis should be carried out for a lattice representing a continuum of anharmonic oscillators. In addition, these theories deal with a very interesting problem in solid state physics, namely the kinetics of phase transitions. Phase transitions are investigated from the point of view of the instability of the crystal lattice with respect to certain oscillation modes. This problem is common to phase transitions not only in ferroelectrics but also in other crystals. The ideas of this theory have exerted a fruitful influence on the development of experimental research by the methods of infrared spectroscopy, light scattering, inelastic slow-neutron scattering, the Mossbauer effect, etc.

In connection with the vigorous development of quantum electronics and nonlinear optics, the electrooptical properties of ferroelectrics turn out to be very interesting research objects since ferroelectric crystals have a large optical nonlinearity and are therefore widely used in these branches of technology.

In recent years, many new research procedures have helped understand the nature of the interaction forces and the energy spectrum of crystals. Radiospectroscopic methods, microwave techniques extending to the millimeter band, far-infrared optics, hypersound, slow neutrons, modern x-ray structure analysis, and high pressures have made it possible to gain a deeper understanding of the nature of ferroelectric phenomena, including those occurring in many new crystals.

Ferroelectricity is the subject of a number of monographs and reviews (see, for example, <sup>[9-13]</sup>). The present review attempts to describe the modern notions concerning the nature of ferroelectricity and to systematize certain of the latest research results in this field. The authors have attempted to consider in greater detail those results which, in their opinion, better illustrate the modern notions concerning the nature of spon-

aneous polarization and features of the dynamics of the ferroelectric crystal lattice. The authors did not intend to cover the results of investigations of the majority of ferroelectrics. This review does not touch upon problems in crystal and domain structure, polarization-reversal processes, investigations of defects, the influence of irradiation, and a few other problems.

## II. MODERN CLASSIFICATION OF FERROELECTRICS

By now there are many known ferroelectrics, such as oxides, sulfates, tartrates, etc., which crystallize into various structures. The variety of types of ferroelectrics makes it difficult to classify them. We can attempt to classify ferroelectrics in the following manner: 1) ferroelectrics that are predominantly ionic crystals or simply ionic ferroelectrics, and 2) ferroelectrics that contain dipole groups in their lattices, including some with hydrogen bonds, or dipole ferroelectrics. The crystals of the second type contain groups of atoms which are bound to each other by covalent bonds. The electron density in them is asymmetrically distributed and therefore these groups have dipole moments. The interaction between the groups is weaker than within each group. If the groups have a charge, then the bonds in the crystal are mainly ionic. In many cases, particularly if individual molecules exist in isolated fashion in the structure, the dipole-dipole interaction and the van der Waals coupling become significant. This separation, which is a manifestation of the unique character of the interaction forces in crystals, determines also the nature of the arising spontaneous polarization. In ionic crystals there are no ready-made dipoles, and the spontaneous polarization is due to a displacement of the anharmonically oscillating ions from the equilibrium position (relative to the positions in the paraelectric phase). In this case the Curie-Weiss constant  $C$  in the Curie-Weiss law for the dielectric constant  $\epsilon = C/(T - \Theta)$  turns out to be large ( $\sim 10^5$  K). A phase transition from the paraelectric state into the ferroelectric state occurs as a result of displacement of the ions, hence the designations phase transitions of the displacement type and ferroelectrics of the displacement type. A classical example of a ferroelectric of this type is barium titanate ( $C \sim 1.5 \times 10^5$  K).

In crystals of the second type there are ready-made dipoles with several equilibrium positions, corresponding to different orientations of the dipoles. The model of such a crystal is actually equivalent to the model of jumping ions which have several equilibrium positions within the confines of the unit cell. In the paraelectric region, the dipoles have a disordered distribution, and order sets in in the ferroelectric region. Hence the designations order-disorder ferroelectric and order-disorder phase transition. In this case, the Curie-

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Weiss constant amounts to approximately  $10^3$  °K. A typical ferroelectric of this kind is sodium nitrite.

This is not the only way to classify ferroelectrics. They can be classified also in accordance with the character of the phase transition from the nonpolar to the polar phase (first or second order), in accordance with the presence or absence of a symmetry center in the paraelectric phase, in accordance with the number of directions of the spontaneous polarization (uniaxial and multiaxial), and in accordance with crystal-chemical attributes.

### III. DEVELOPMENT OF THERMODYNAMIC THEORY

The phenomenological theory,<sup>[2,4]</sup> according to which the thermodynamic potential of a ferroelectric crystal is represented in the form of an expansion in terms of a certain small parameter, chosen to be the polarization, is equivalent from the microscopic point of view to the zeroth self-consistent field approximation. The possibility of such an expansion of the thermodynamic potential is generally speaking not clear. In those cases when the occurrence of spontaneous polarization is connected with the change in the number of atoms in the unit cell, the phase transition, within the framework of the general Landau theory, cannot be described solely with the aid of the polarization vector.<sup>[15,16]</sup> An example of such a transition is the transition in ammonium fluoroberyllate.<sup>[17]</sup> But even if the number of atoms in the cell does not change during the transition, there are grounds for expecting the thermodynamic potential to have a singularity near the Curie temperature.

The expansion of the thermodynamic potential, in accordance with<sup>[2-4]</sup>, is of the form

$$\Phi(p, T, \eta) = F + \alpha\eta^2 + \frac{\beta}{2}\eta^4 + \frac{\gamma}{6}\eta^6 + \dots + \delta(\text{grad } \eta)^2,$$

where  $p$ —pressure,  $T$ —temperature,  $\alpha, \beta, \gamma$ —coefficients in the expansion, and  $\eta$ —ordering parameter introduced in the theory of Landau phase transitions, which in this case has the meaning of the lattice polarization. The term  $\delta(\text{grad } \eta)^2$  describes the fluctuations of  $\eta$  (polarization), which should play the most significant role in the region of the Curie temperature.<sup>[4]</sup> This is confirmed experimentally. In particular, the Landau theory, like the Ginzburg-Devonshire theory, cannot explain, without taking into account the fluctuation term, all the experimental data concerning the character of the anomaly of the specific heat at the Curie point (see, for example,<sup>[18-20]</sup>).

Recently, several attempts were undertaken to discuss the applicability of the phenomenological theory and to calculate the corrections to the zeroth self-consistent field approximation (see, for example,<sup>[4, 21, 22]</sup>). In<sup>[22]</sup>, a method is described for finding the corrections in the form of a series in  $r_0^{-3}$ , where  $r_0$  is the ratio of the interaction radius to the average distance between particles.

The larger the interaction radius, the closer to the transition point is the phenomenological theory applicable. That is to say, the electromagnetic dipole interaction leads to a broadening of the region of applicability of the phenomenological theory, and to a decrease of the corrections. In uniaxial ferroelectrics in the case of

dipole-dipole interaction, on approaching the Curie temperature, the corrections increase like  $r_0^{-3} \ln |T - T_C|$ , and in the case of finite-radius forces they increase like  $r_0^{-3} |T - T_C|^{-1/2}$ . A microscopic approach to thermodynamics is now being developed.<sup>[23,24]</sup>

In<sup>[25,26]</sup>, a more accurate expression was obtained for the coefficients in the expansion of the thermodynamic potential in terms of the microscopic quantities, and correlation effects were discussed under the assumption of small anharmonicity, which admits of the independence of phonons with different wave vectors. It is shown that the general results and the form of the temperature dependences remain the same as under the assumption that the correlation between cells is small<sup>[22]</sup> and in the phenomenological theories.

The results of<sup>[4, 6, 21-28]</sup> explain why the simple thermodynamic theory without allowance for the fluctuation effects turns out to be in most cases sufficiently accurate for the description of the results of the experiment even near a phase transition.

### IV. BASIC CONCEPTS OF THE DYNAMIC THEORY OF FERROELECTRICITY AND ITS EXPERIMENTAL VERIFICATION WITH THE AID OF AN INVESTIGATION OF THE OPTICAL SPECTRA AND INELASTIC NEUTRON SCATTERING

The dynamic theory of ferroelectricity is a development of the Born and Huang dynamic theory of the crystal lattice.<sup>[8]</sup> The principles of the dynamic theory of ferroelectricity were developed in the papers by Ginzburg, Anderson, and Cochran.<sup>[2-7]</sup> These concepts were subsequently developed further by Cowley, Silverman, Janovec, Vaks, Larkin, and others.<sup>[25-33]</sup> A review of papers on the dynamics of crystal lattices of ferroelectrics is contained in<sup>[34,35]</sup>. The ferroelectric transition is regarded as a result of instability of the crystal lattice to one of the modes of the transverse optical oscillations with wave vector  $\mathbf{q} = 0$ . The frequency  $\omega$  of this mode decreases with decreasing temperature and tends to zero at the transition point.

The condition  $\omega^2 \sim (T - \Theta)$  follows from a comparison of the equation of motion of the anharmonic oscillator and the condition of the minimum of the thermodynamic potential.<sup>[4]</sup>

Cochran<sup>[7]</sup> carried out a more correct calculation of the polarizabilities and of the interaction forces using the Dick-Overhauser shell model.<sup>[36]</sup> The equation of motion of the cores and of the external electron shells is given in<sup>[7]</sup> (the cores are made up of nuclei and the inner electron shells). The secular equation yields all the frequencies, which should be real. If one of the frequencies ceases to be real, then the amplitude of the oscillation increases in time, the lattice becomes unstable, and a phase transition takes place.

In the case of acoustic oscillations, no dipole moments are produced and therefore optical oscillations with small wave vector  $\mathbf{q}$  are of interest from the point of view of the ferroelectric phase transition, i.e., with very large wavelength. Otherwise compensation of the dipole moments takes place in small regions of the crystal, and the crystal does not have a macroscopic dipole moment. In addition, it is known that the frequency of the longitudinal optical oscillations is always high-

er than the frequency of the transverse optical oscillations ( $\mathbf{E}_{\text{macr}} \perp \mathbf{q} = 0$  when  $\mathbf{q} = 0$ , and, for example, for diatomic cubic crystals,  $\mathbf{E}_{\text{macr}} \parallel \mathbf{q} = -4\pi\mathbf{P}$ ). Therefore only the frequency of the transverse optical mode with  $\mathbf{q} = 0$  can vanish, corresponding to the ferroelectric phase transition.

This consideration can be obtained from the well known dispersion formula

$$\frac{\epsilon_0}{\epsilon_\infty} = \frac{\omega_i^2}{\omega_T^2}$$

as  $\omega_T \rightarrow 0$  and  $\epsilon_0 \rightarrow \infty$ . According to Cochran

$$\omega_T^2 \mu = R'_0 - \frac{4\pi}{9v} (Z'e)^2 (\epsilon_\infty + 2),$$

where  $\mu$  is the reduced mass,  $R'_0$  the force constant of the short-range restoring forces, and  $Z'e$  is the effective charge.

The meaning of this equation corresponds to the statement by Ginzburg and Slater that the condition for the ferroelectric phase transition is compensation of the short-range restoring forces and of the long-range electrostatic forces,<sup>[2, 37]</sup> but only for the given oscillation mode.

To obtain the Curie-Weiss law for  $\epsilon_0$  and consequently for  $\omega_T^2$ , Cochran proposed that in the region of the transition the quantity

$$1 - \frac{4\pi}{R'_0 9v} (Z'e)^2 (\epsilon_\infty + 2)$$

is proportional to  $Q - T_C$  ( $T_C$ —Curie temperature).

Such a temperature dependence can be obtained for  $\omega_T^2$  more rigorously by taking into account the anharmonicity of the oscillations. Several attempts to take the anharmonicity into account were made. A one-dimensional chain model was considered in<sup>[29]</sup>. At small values of the wave vector  $\mathbf{q}$ , the frequency of the "ferroelectrically active" mode remains positive because of the contribution of the anharmonic interaction, the magnitude of which depends strongly on the temperature. This indeed determines the strong temperature dependence of the frequency of the ferroelectrically active mode at small values of  $\mathbf{q}$ .

In<sup>[28]</sup>, the temperature dependence of the frequency of the ferroelectrically active mode was calculated more rigorously as applied to  $\text{SrTiO}_3$ . In<sup>[31-33]</sup> it is shown that the electron polarization has a strong influence on the conditions for the instability of the soft mode: allowance for the electron polarizability facilitates the vanishing of the frequency of this mode.

Attempts have been made recently to connect theoretically the magnitude of the electron polarizability with the lattice vibrations. To this end, investigations are made of the dependence of the electronic band structure on the lattice vibrations (see the review<sup>[35]</sup>). The band structure of  $\text{SrTiO}_3$  was investigated theoretically in<sup>[38]</sup>, and it was found that the ion displacements greatly influence the magnitude of the smallest energy gap between the valence band made up of the oxygen 2p electrons and the conduction band made up of the titanium 3d electrons. An increase of the width of the gap during polarization causes a change in the electron polarizability, decreasing its magnitude. In<sup>[39]</sup>,

an attempt was made to calculate theoretically the magnitude of this electrooptical effect. Order-of-magnitude agreement was obtained for this quantity with the results of measurements of the electrooptic effect in a number of crystals with perovskite structure (see Ch. VII).

It was proposed in<sup>[7]</sup> that the phase transition to the antiferroelectric state is a result of the vanishing of the frequency of a transverse optical mode with wave vector  $\mathbf{q} = (\frac{1}{2}, 0, \frac{1}{2})$  (on the boundary of the Brillouin zone). This corresponds to "freezing" of the antiparallel motion of ions of the same type in neighboring cells on going over to the antiferroelectric phase, in which static antiparallel ion displacements are observed.

The idea of using structure information concerning the low-temperature phase to draw conclusions concerning the dynamics of a phase of higher symmetry has been developed in<sup>[40]</sup>. It was concluded there that several oscillation modes take part simultaneously in the phase transition into the antiferroelectric state of such antiferroelectrics as  $\text{PbZrO}_3$  and  $\text{NaNbO}_3$ . The opinion was expressed in<sup>[41]</sup> that a low-frequency "ferroelectrically active" mode with  $\mathbf{q} \rightarrow 0$  should be observed in the paraelectric phase of antiferroelectrics, and this mode determines satisfaction of the Curie-Weiss law for  $\epsilon$ . However, when the temperature is lowered, the lattice becomes unstable with respect to the antiferroelectric mode with  $\mathbf{q}$  lying on the Brillouin zone boundary before the frequency of the "ferroelectrically active" mode vanishes.

We now consider the available experimental results of investigations of the optical spectra and of inelastic neutron scattering, in which data were obtained on the low-frequency "ferroelectrically active" lattice vibrations, without dealing with investigations of other regions of the spectra.

Investigations of the infrared spectra by the reflection method have made it possible to observe the ferroelectrically active mode and to investigate its temperature dependence in a number of ferroelectrics.<sup>[42-46]</sup> This mode was first observed in single-crystal strontium titanate.<sup>[42]</sup> At room temperature, it lies in the region of  $100 \text{ cm}^{-1}$ , and at  $93^\circ \text{K}$  in the region of  $50 \text{ cm}^{-1}$ . The relation  $\omega_T^2 = A(T - T_C)$  is satisfied. Such a mode

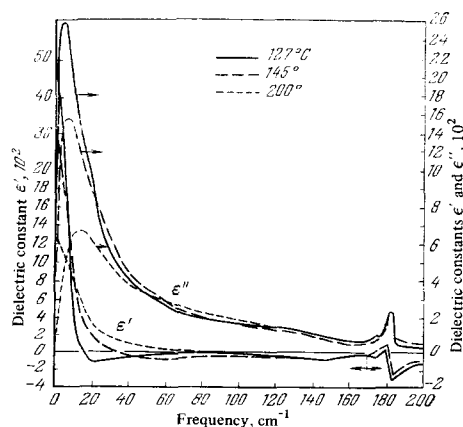


FIG. 1. Dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) part of the dielectric constant of single-crystal  $\text{BaTiO}_3$  on the frequency at different temperatures (from<sup>[46]</sup>).

was observed also in the paraelectric phase of barium titanate, and the frequency of this mode satisfied the same relation. A large oscillator strength and a high degree of anharmonicity were noted. Figure 1 shows the dependence of  $\epsilon'$  and  $\epsilon''$  on the frequency in single-crystal  $\text{BaTiO}_3$  for different temperatures, in accordance with [46]. An estimate of the frequency of the ferroelectrically active mode depends on the model used in the calculation, and the results of [43] and [46] differ by a factor of approximately 3.

The temperature dependence of the frequency of the ferroelectrically active mode was recently measured in potassium tantalate.[47] The frequency of this mode changes from  $106 \text{ cm}^{-1}$  at  $463^\circ \text{K}$  to  $26 \text{ cm}^{-1}$  at  $12^\circ \text{K}$ , and good quantitative agreement is observed between the temperature dependence of the square of the frequency and  $1/\epsilon$ .

The ferroelectric oscillation determines more than 90% of all the polarization of the investigated crystals with perovskite structure, and the main contribution (65–80% for  $\text{BaTiO}_3$  [45]) is made by the electron polarization. Thus, the ferroelectrically active oscillation has a complicated electron-ion character, which agrees with the recently developed concepts regarding the dependence of the electronic band structure of the crystals on the displacements of the ions.[38]

In accordance with the idea that the spontaneous polarization has the same nature in ferroelectrics and antiferroelectrics, a low-frequency oscillation determining approximately 90% of the entire polarization was likewise observed in the antiferroelectric lead zirconate.[48]

From among the attempts to observe the ferroelectrically active mode in ferroelectrics of other groups by investigating infrared spectra, mention can be made of [49], where an investigation of reflection in  $\text{KH}_2\text{PO}_4$  revealed a smeared-out band in the region  $10\text{--}100 \text{ cm}^{-1}$ , and [50], where a study of absorption in powdered  $\text{KH}_2\text{PO}_4$  revealed an absorption band with a center in the region of  $50 \text{ cm}^{-1}$ . It is shown in both papers[49, 50] that the band shifts towards lower frequencies when the Curie temperature is approached.

Investigations of Raman scattering in ferroelectrics are very complicated, since the lines of the "ferroelectrically active" oscillations are close to the exciting line, and become smeared out, in agreement with Ginzburg's theoretical predictions.[4, 5, 51] It is also very difficult to prepare sufficiently transparent samples. Therefore the results of various authors differ greatly from one another, and we shall not discuss them in detail. In an investigation of single-crystal  $\text{BaTiO}_3$ , [52] a strong temperature dependence of one of the oscillations, with a frequency that varied from  $230 \text{ cm}^{-1}$  at the Curie point to  $261 \text{ cm}^{-1}$  at  $5^\circ \text{K}$ , was observed. It was concluded that this oscillation is a longitudinal optical mode connected with the low-frequency transverse mode by the modified Liddén-Sachs-Teller relation.[27] An estimate based on this relation gives for the transverse ferroelectrically active mode at the Curie point a frequency of  $16 \text{ cm}^{-1}$ . Figure 2 shows the temperature dependence of the considered longitudinal mode as given in [52].

In the investigation of the Raman scattering spectra of  $\text{KH}_2\text{PO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ , [53] a line was observed in the

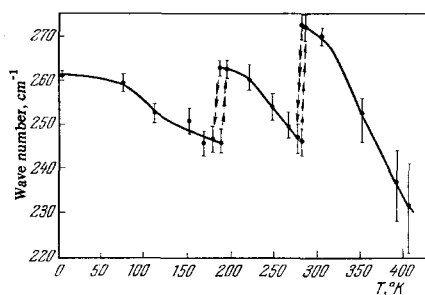


FIG. 2. Temperature dependence of the frequency of the longitudinal optical mode in barium-titanate crystal (from [52]).

vicinity of  $34 \text{ cm}^{-1}$ . This line was shifted towards the exciting line on approaching the Curie temperature, in agreement with data on the infrared spectra.[49, 50] It was observed in [54] that when  $\text{KH}_2\text{PO}_4$  goes through the Curie point the bands lying in the region of  $155$  and  $188 \text{ cm}^{-1}$  experience a temperature shift, certain lines become narrower, and new groups of lines appear in the ferroelectric phase. However, the spectrum of  $\text{KH}_2\text{PO}_4$  cannot yet be regarded as completely interpreted.

In investigations of the Raman spectrum of  $\text{NaN}_2$ , [55–57] a decrease was observed in the frequency near the Curie temperature in the case of  $153 \text{ cm}^{-1}$  line, which corresponds to orientation oscillation of the  $\text{NO}_2^-$  anion around the  $a$  axis. It is proposed in [57] that this oscillation is ferroelectrically active. However, the decrease of the frequency of this oscillation does not suffice to explain the large values of  $\epsilon$  near the Curie point. In view of the fact that reorientation around the  $a$  axis leads to a shift of the centers of gravity of the anions relative to the cations of  $\text{Na}^{1+}$  around the  $b$  axis, one should expect in  $\text{NaN}_2$ , in accordance with [57], a decrease in the frequency of the corresponding translational oscillation that contributes to  $\epsilon$ .

Very interesting results on the ferroelectric lattice dynamics were obtained with the aid of inelastic scattering of slow neutrons. Great interest attaches to investigations of single crystals, in which it is possible to obtain the dispersion curves  $\omega = \omega(\mathbf{q})$ , where  $\omega$  are the frequencies of the normal modes and  $\mathbf{q}$  is the wave vector. In the investigation of polycrystalline samples, the contribution made to the spectrum by the low-frequency optical branch is distributed over a broad frequency interval, and its separation entails serious difficulties. Therefore inelastic scattering of neutrons by polycrystalline  $\text{BaTiO}_3$ , [58, 59]  $\text{PbTiO}_3$ , and  $\text{SrTiO}_3$  [59] revealed no significant anomalies on going through the Curie point.

Single crystals of strontium titanate were investigated in [60] with the aid of the inelastic coherent scattering of neutrons; dispersion curves  $\omega(\mathbf{q})$  were obtained for different normal oscillations. An inelastic-scattering maximum connected with the ferroelectrically active mode with  $\mathbf{q} \rightarrow 0$ , whose frequency decreased on approaching the Curie temperature, was observed. Figure 3 shows the temperature dependence of the square of the frequency of this mode and of  $1/\epsilon$  (taken from [61, 62]), which confirms the prediction of the dynamic theory.[17] An interesting explanation was obtained in [60] for the nature of the phase transition in  $\text{SrTiO}_3$  at  $110^\circ \text{K}$ , which according to [60] is the result

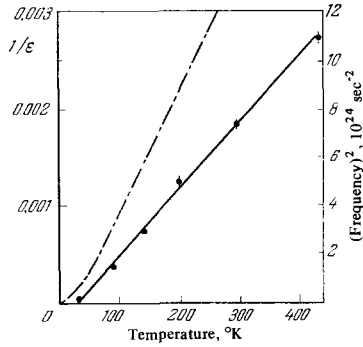


FIG. 3. Temperature dependence of the square of the frequency of the ferroelectrically active mode (solid line) and  $1/\epsilon$  (dashed line) in  $\text{SrTiO}_3$  (from [60];  $\epsilon$  taken from [61,62]).

of the random degeneracy of the "ferroelectrically active" branch of the transverse optical oscillations and the longitudinal acoustic branch.

A soft optical mode was recently observed with the aid of inelastic scattering of neutrons in the paraelectric phase of single crystals of  $\text{KTaO}_3$  [63] and  $\text{BaTiO}_3$ . [64] In the authors' opinion, the ferroelectrically-active transverse optical mode has in  $\text{BaTiO}_3$  a lower frequency than the transverse acoustic mode, with the exception of the region of very small  $q$ . The energy of the soft mode decreases with decreasing temperature, from 1.4 meV at 430°C to 0.8 meV at 230°C, and the following relation holds:

$$h^2\omega_{TO}^2 = A \cdot 10^4 (\epsilon \approx k(T - T_0)).$$

The values of  $A$  are  $\sim 0.11 (\text{meV})^2$  in  $\text{BaTiO}_3$ ,  $\sim 3.7 (\text{meV})^2$  [42, 60] in  $\text{SrTiO}_3$ , and  $\sim 2.8 (\text{meV})^2$  in  $\text{KTaO}_3$ . [47, 63]

It should be noted that at the present time it is not quite clear to what degree the concepts of the existing dynamic theory are applicable to ferroelectrics with order-disorder phase transition, especially those of them in which the hydrogen bonds play an active role. Recognizing that in most such crystals the transitions are connected not only with the ordering of the ready-made dipole moments, but also with ion shifts that lead to realignment of the lattice, it can be assumed that the main concepts of the dynamical theory remain in force.

## V. RADIO SPECTROSCOPICAL INVESTIGATIONS AND INVESTIGATIONS WITH THE AID OF THE MOSSBAUER EFFECT

### 1. Electron Paramagnetic Resonance

The EPR on impurities of certain paramagnetic ions contained in the crystal lattice (with an impurity content usually amounting to a fraction of 1%) was investigated in a number of ferroelectrics. In addition, attempts were made to investigate with the aid of EPR the crystal-lattice defects produced, for example, when a number of oxygen-containing ferroelectrics are reduced.

The most frequently employed paramagnetic impurity are ions with half-filled  $d$  or  $f$  shells in the  $S$  state. These are usually  $\text{Fe}^{3+}$  or  $\text{Mn}^{2+}$  ions, the ground state of which is  ${}^6S_{5/2}$ , or  $\text{Gd}^{3+}$  or  $\text{Eu}^{2+}$  ions in the state  ${}^8S_{7/2}$ . The EPR was investigated in greatest detail in

ferroelectrics with the perovskite structure. We shall therefore illustrate the possibilities of the EPR method using barium titanate as an example.

The first to study the EPR spectrum in barium-titanate crystals were Hornig et al., [65] who found that the spectrum is due to  $\text{Fe}^{3+}$  impurity ions in the ground State  ${}^6S_{5/2}$ , replacing the  $\text{Ti}^{4+}$  ions. EPR in tetragonal and cubic phases on  $\text{Fe}^{3+}$  was investigated in [65-68]. In the tetragonal phase, the Hamiltonian for  $\text{Fe}^{3+}$  is of the form [65]

$$\mathcal{H} = g\beta\mathbf{H}\mathbf{S} + DS_z^2 + aS_x^2 + b(S_x^2 + S_y^2),$$

where the first term describes the Zeeman splitting of the ground state in a magnetic field  $\mathbf{H}$  with isotropic splitting factor  $g$ ,  $\beta = eh/4\pi mc$ ,  $e$  and  $m$  are the charge and mass of the electron,  $c$  is the velocity of light,  $h$  is Planck's constant, and  $S$  is the ion electron spin operator. The second term is due to the tetragonal component of the crystal field. In the cubic phase  $a = b$  and  $D = 0$ . In the positions occupied by the  $\text{Fe}^{3+}$  ions, the crystal field has axial symmetry, and the  $z$  axis of the axial field coincides with the tetragonal  $c$  axis of the crystal. Thus, the symmetry of the nearest surroundings of the  $\text{Fe}^{3+}$  ions, and consequently, as can be assumed, also of the  $\text{Ti}^{4+}$  ions, coincides with the tetragonal symmetry of the lattice.

The EPR spectrum in barium titanate crystals doped with  $\text{Ge}^{3+}$  was investigated in [69, 70]. The spin Hamiltonian for the tetragonal phase, according to [69], is of the form

$$\mathcal{H} = g\beta\mathbf{H}\mathbf{S} + b_{2,0}O_{2,0} + b_{4,0}O_{4,0} + b_{4,4}(O_{4,4} + O_{4,-4}) + b_{6,0}O_{6,0} + b_{6,4}(O_{6,4} + O_{6,-4}).$$

In the cubic phase  $b_{2,0} = 0$ ,  $b_{4,4} = [70^{1/2}/14]b_{4,0}$ , and  $b_{6,4} = -[14^{1/2}/2]b_{6,0}$ . The first term of the Hamiltonian is the Zeeman energy with isotropic splitting factor  $f$ . The other terms describe the interaction of the spin  $S$  with the crystal field.  $O_{lm}(S)$  are spin-dependent operators that transform like spherical harmonics upon rotation.

The  $\text{Gd}^{3+}$  ions replace in the lattice mainly the  $\text{Ba}^{2+}$  ions; it is therefore natural that in the tetragonal phase the crystal field acting on the  $\text{Gd}^{3+}$  ions has an axial symmetry and the axial axis coincides with the tetragonal  $c$  axis. It should be noted, that besides the seven lines for the  $\text{Gd}^{3+}$  ions at the  $\text{Ba}^{2+}$  sites, there is observed also a cubic spectrum, which is ascribed in [70] to the  $\text{Gd}^{3+}$  in the positions of  $\text{Ti}^{4+}$ , since the large  $\text{Gd}^{3+}$  ions, on entering into the octahedron, should move the oxygen ions apart, and therefore the axial component of the field should vanish.

Investigations of EPR on  $\text{Mn}^{2+}$  ions were made in [71, 73]. In the tetragonal phase, the crystal field acting on the  $\text{Mn}^{2+}$  has axial symmetry. It is assumed [73] that the  $\text{Mn}^{2+}$  ions replace more readily the  $\text{Ba}^{2+}$  than the  $\text{Ti}^{4+}$  ions, but this can hardly be regarded as finally proven.

There are many reports of investigations of the temperature dependence of the EPR spectrum (see, for example, [67-69, 74]). By way of an example, Fig. 4 shows the temperature dependence of the resonant magnetic fields in the tetragonal phase of  $\text{BaTiO}_3$  doped with  $\text{Gd}^{3+}$ . [69] The largest temperature dependence was observed for  $D$  and  $b_{20}$ .

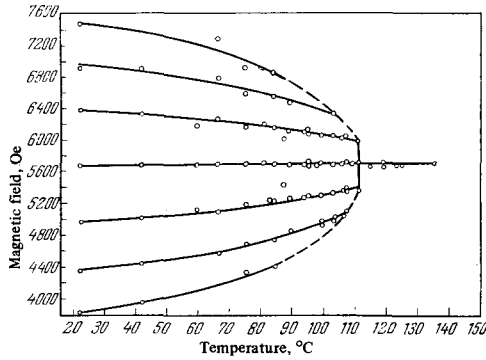


FIG. 4. Temperature dependence of the resonant magnetic field in EPR observations in the tetragonal phase of barium titanate doped with  $Gd^{3+}$  (from [69]).

Great interest attaches to attempts to connect the axial and cubic parameters of the spin Hamiltonian with the coefficients of the crystal-field potential  $V_{cryst}$ , which, as is well known, can be represented in the form of an expansion in spherical harmonics

$$V_{cryst} = A_2^0 Y_2^0 + A_4^0 r^4 [Y_4^0 + (5/14)^{1/2} [Y_4^4 + Y_4^{-4}]] + \dots$$

The first term describes the axial field and is designated  $V_{ax}$ , and the second the cubic field and is designated  $V_{cub}$ .

The problem of determining the splitting of the ground S state under the influence of the crystal field is quite complicated and has not yet been finally solved. The pure S state should not be split by either the crystal field or by the spin-orbit interaction, and the experimentally observed splitting offers evidence of the need for taking into account the admixture of different excited states. The problem of the splitting of the  $^6S_{5/2}$  state was considered in [75-79]. Various schemes for the perturbation of the ground state of  $Gd^{3+}$  were discussed, for example, in [80]. The contributions of different axial-splitting mechanisms turned out to be proportional to either the first or the second power of the axial potential of the crystal field. According to [77]

$$D = \alpha V_{ax} + \beta V_{ax}^2.$$

A calculation that starts out from the model of point-like charges and dipoles (see, for example, [69]) shows that for the barium-titanate lattice the change of the axial potential at the  $Ba^{2+}$  or  $Ti^{4+}$  position, on going over to the tetragonal phase, depends on  $\delta a/a$ , where  $a$  is the lattice constant, and also on terms of the type  $(\delta z_i/a)^2$ , where  $\delta z_i$  are the displacements of the ions from the positions in the cubic phase. The quantity  $\delta a/a$  is proportional in this case to the square of the spontaneous polarization, since the lattice deformation  $\delta a/a$  in the barium titanate is by its nature the result of electrostriction (there is no piezoeffect in the paraelectric phase of barium titanate). The terms  $(\delta z_i/a)^2$  are also proportional to  $P_s^2$ .

Experiment yielded for barium titanate a linear connection between the axial parameter of the Hamiltonian at the square of the spontaneous polarization, and also  $\delta a/a$  (Fig. 5), showing that the contribution of the quadratic term of the axial potential to the axial parameter of the Hamiltonian is small.

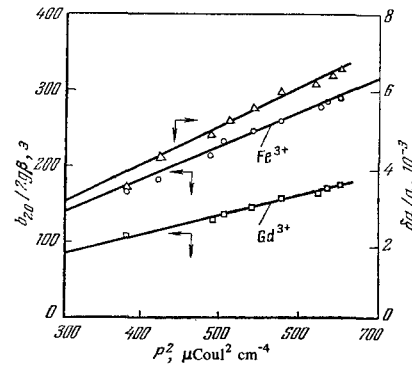


FIG. 5. Dependence of the axial parameter of the spin Hamiltonian in tetragonal barium titanate doped with  $Fe^{3+}$  and  $Gd^{3+}$ , and of the tetragonal lattice distortion  $\delta a/a$ , on the square of the spontaneous polarization  $P_s^2$  (from [69]).

The Mossbauer effect on  $Fe^{57}$  was used in [78] to measure the quadrupole splitting in a number of compounds, and the field gradient, which is proportional to the crystal-field parameter  $A_2^0$ , was compared with the axial parameter  $D$  known from EPR investigations. In other words, the relation between  $D$  and  $V_{ax}$  was measured experimentally. However, the large scatter of the points hardly allows any conclusions to be drawn with respect to the applicability of the existing theories.

In [81], an attempt was made to relate the temperature dependence of the splitting of the crystal field in  $SrTiO_3$  with the presence of a "soft" ferroelectrically-active mode contributing to the temperature dependence of the term  $b_{4,0}$ . However, in the investigation of EPR on  $Gd^{3+}$  in  $KTaO_3$ , [82] a very small temperature variation of  $b_{4,0}$  was found, although from the point of view of a crystal-lattice dynamics,  $SrTiO_3$  and  $KTaO_3$  are close to each other. Therefore the question of the influence of the ferroelectrically-active mode on the temperature dependence of  $b_{4,0}$  remains open.

Another interesting trend in the study of ferroelectrics with the aid of EPR is the investigation of the crystal-lattice defects. Many attempts were made to investigate with the aid of EPR the crystal-lattice defects of barium titanate.

In some investigations, EPR signals were observed in reduced barium titanate containing certain impurities ascribed to F centers (crystal-lattice vacancies that have captured one electron) (see, for example, [82-85]). However, no signals corresponding to singly-charged vacancies were observed in [86, 87]. Therefore the question of the existence of such vacancies in barium titanate still remains unanswered (see also [88]).

Investigations of EPR in ferroelectrics with lower symmetry have progressed less than in the case of perovskites. This apparently is due to the complexity of the interpretation of the results. Research on perovskites was aided also by the possibility of observing a clearly pronounced temperature dependence of the splitting when the degeneracy is lifted as a result of the phase transition from the cubic phase into a phase of lower symmetry, making it possible to determine small deviations from cubic symmetry. On the other hand, the splitting changes much less in the case of a transition between phases with lower symmetry.

In many ferroelectrics with lower symmetry, EPR was used to investigate the free radicals produced as a result of irradiation; this has made it possible to determine the number of non-equivalent positions of the free radicals in the unit cell, the change of this number on going through the Curie point, the form and dynamics of formation of the free radicals, etc.

EPR investigations in irradiated Rochelle salt were carried out, for example, in [89, 90]. Investigations of the EPR on  $\text{Cu}^{2+}$  impurity ions in triglycine sulfate and Rochelle salt [91, 92] have made it possible to obtain certain information on the causes of the "fixing" of the spontaneous polarization in these ferroelectrics when  $\text{Cu}^{2+}$  is introduced, a phenomenon manifest in the appearance of double hysteresis loops, increase of the coercive force, etc. [93]

In conclusion it should be noted that investigations of EPR in ferroelectrics yield valuable information concerning the lattice symmetry at the location of the paramagnetic impurity and concerning the changes of the symmetry, help determine the character of the substitution of the impurity, its location in the lattice, etc., but at the present time these investigations hardly reflect the distinguishing features of the occurrence of spontaneous polarization.

## 2. Nuclear Magnetic Resonance

The greatest progress in the investigation of NMR in ferroelectrics has been the result of the study of ferroelectrics with hydrogen bonds experiencing order-disorder phase transitions, to which a large number of NMR investigations have been devoted. Investigations were made also of other nuclei. NMR investigations have made it possible, in many cases, to refine the crystal structure in the character of the chemical bond, to determine the positions of the resonating nuclei, to investigate the character of the ferroelectric phase transition, etc.

The chemical shift on  $\text{Pb}^{207}$  nuclei was investigated in [94] for a number of ferroelectrics and antiferroelectrics with perovskite structure. The magnitude of the observed chemical shift ( $\sim 1.2\%$ ) indicates appreciable covalence of the chemical bond of the lead ions in these compounds. No change of the chemical shift was observed at the Curie point of lead zirconate and of one of its solid solutions. This demonstrates that the ferroelectric or antiferroelectric phase transition is not connected with a large change of the covalence of the bonds of the lead ions.

A change in the second moment of the resonance line in a ferroelectric phase transition was first observed by Losche [95] in the upper Curie point of Rochelle salt, in investigations of proton resonance. It was shown in [96] that at the lower Curie point in Rochelle salt no noticeable change occurs in the second moment, thus indicating that the phase transitions in Rochelle salt have a different character. In addition, it was reported in [96] that the second moment changes at  $T_C$  in potassium ferrocyanide, and it was shown that its ferroelectric properties are closely connected with the ordering of the dipole moments of the water of crystallization. [97-99]

Investigations of NMR in dicalcium strontium propionate [100] have led to the conclusion that the occurrence

of spontaneous polarization in this compound is connected with violation of the flat structure of the propionate acid ion ( $\text{CH}_3\text{CH}_2\text{COO}$ ). This is analogous to some degree to the mechanism of occurrence of spontaneous polarization in triglycine sulfate. Very interesting results were obtained in the investigation of NMR on protons and fluorine nuclei in ferroelectrics of the triglycine sulfate (TGS) group. [101-104] It turned out that small changes of the line width occur at the Curie point in spite of the appreciable deceleration of the motion of the resonating nuclei at these temperatures (see below), this being due to the fact that the characteristic frequencies of the internal motion at the investigated temperatures are higher than the frequency of the Larmor precession of the nuclei. The observed small linewidth changes in TGS are thus attributed not to the "freezing" of the internal motion, but to static reorientation of the glycine groups. Therefore special interest attaches to investigations of NMR on deuterons having quadrupole moments. Investigations of NMR and of the quadrupole splitting of the NMR lines in deuterated triglycine sulfate [105, 106] have made it possible to determine more accurately the roles played in the ferroelectric phase transition by each of the three glycine groups that enter in the TGS molecule. It is shown in [106] that in the paraelectric phase the deuterons of groups GII and GIII jump backward and forward along the bond, with a frequency larger than the frequency of the quadrupole splitting, while below the Curie point they "freeze" at the GIII groups. It is shown further that the glycine group GI in the paraelectric phase is not distributed statistically above and below the mirror plane at  $b = 1/4$  and  $b = 3/4$ , as was assumed in [107], but lies in this plane. Large but gradual changes of the tensor of the field gradient in GI upon cooling below the Curie temperature offer evidence of a gradual displacement of the GI group from the mirror plane into its own low-temperature position obtained in [107]. Thus the NMR data show that the ferroelectric transition in TGS should be regarded as a combination of order-disorder transitions of the protons OIII-H-OH and the glycine groups GII and GIII and a transition of the displacement type for the groups GI.

Investigation of NMR in deuterated potassium dihydrophosphate [105] has shown that on going through the Curie point no significant shifts of the average point of the resonant line is observed, i.e., the tensor of the electric-field gradient does not change essentially. In the paraelectric phase, the deuterons jump rapidly along the short O-D-O bond from one position of equilibrium to another. On going over to the ferroelectric state, the jump time increases by eight orders of magnitude (Fig. 6), i.e., a large increase of the activation energy is observed for the deuteron jumps. This in turn determines the processes of "freezing" of the dipole groups on going over into the ferroelectric state. Similar results were obtained recently in the investigation of deuteron resonance in the antiferroelectric  $\text{ND}_4\text{D}_2\text{PO}_4$ . [108] Additionally splitting of the NMR line is interpreted as a result of ordering of the deuterons in bonds between the phosphate ions.

Investigations of NMR in ammonium sulfate ( $\text{NH}_4$ )<sub>2</sub>SO<sub>4</sub> and in deuterated ammonium sulfate [109] have made it possible to propose for the ferroelectric

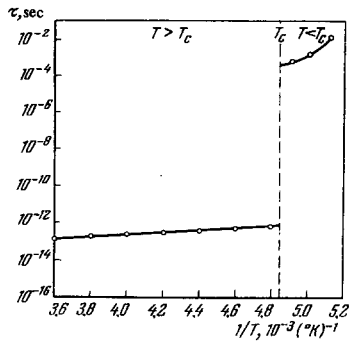


FIG. 6. Temperature dependence of the time of jumping of the deuterons along the O-D-O bonds in  $\text{KD}_2\text{PO}_4$  (from [106]).

transition a mechanism connected with the ordering of the  $\text{NH}_4^+$  groups that have two non-equivalent positions with respect to one of the crystallographic planes—the (a, b) plane.

Among the investigations of NMR on various nuclei, many are devoted to ferroelectrics containing sodium and lithium ions. In [110] they investigated NMR in Rochelle salt on  $\text{Na}^{23}$  nuclei. Reference 111 is devoted to an investigation of the quadrupole splitting of NMR on the  $\text{Li}^7$  nuclei in several ferroelectrics containing lithium ions (lithium-ammonium and lithium-gallium tartrates, lithium niobate and tantalate). Lithium niobate was investigated also in [112–114]. It has been shown that the asymmetry parameter for  $\text{Li}^7$  is equal to zero, and the constant of the quadrupole coupling was found in [114] to be 53 kHz; the second moment of the resonant curve was determined in [113]. The mechanism of the spin-lattice relaxation is discussed in [113, 114]. It is suggested in [114] that the relaxation mechanism in the investigated crystals is predominantly the quadrupole mechanism. From a comparison of the results of the experimental and theoretical determination of the electric-field gradient from the point-ion model it can be concluded that the chemical bonds in this compound are highly covalent.

NMR in sodium nitrite on  $\text{Na}^{23}$  nuclei was investigated at room temperature in [115]. The temperature dependence of the quadrupole splitting was investigated in [116–118]. Anomalies were observed at the ferroelectric Curie point in the region of  $163^\circ\text{C}$ , and also at  $178^\circ\text{C}$ . In [118], furthermore, it was shown that two different electric-field gradients are observed in the interval where the antiferroelectric phase exists ( $\sim 1^\circ$  above the ferroelectric region). A detailed study of the orientation and temperature dependences of the second moment of the central component of the spectrum was made in [119]. When the magnetic field is oriented parallel to the a axis, a plateau in the temperature dependence is observed in the region  $165\text{--}180^\circ\text{C}$ ; this may be connected with the presence of a certain ordering in this structure.

In [120] they investigated NMR on  $\text{Nb}^{93}$  in potassium niobate, but since the main results of that investigation were obtained in the study of quadrupole splitting of the NMR lines and in the investigation of the quadrupole resonance, this paper will be discussed later.

### 3. Nuclear Quadrupole Resonance

NQR investigations make it possible to determine the tensor of the electric field gradient (the magnitude and orientation of its components and the asymmetry parameters, yielding by an independent method information concerning the symmetry of the crystal structures, the presence of non-equivalent positions of the atoms, their mutual arrangement, the form of the chemical bond, etc. An analysis of the NQR relaxation times makes it possible to judge the character of the internal motion in bodies. Because of the fact that the NQR frequencies are determined by the gradient of the electric field, this method was particularly sensitive to any kind of changes of the crystal fields and therefore makes it possible to yield valuable information concerning the conditions for the occurrence of the ferroelectric state and the character of the ferroelectric phase transitions.

NQR in ferroelectrics has been the subject of very few investigations, this being principally due to the difficulty of growing large good-quality crystals ensuring the possibility of obtaining NQR signals.

The quadrupole splitting of NMR, and also the NQR in  $\text{KNbO}_3$  on the  $\text{Nb}^{93}$  nuclei, were investigated in [120]. The temperature dependence of the NQR spectrum of  $\text{KNbO}_3$  was investigated in detail in [121]. An estimate of various possible contributions to the temperature dependence of the frequencies for  $\text{KNbO}_3$  [121] has shown that the temperature dependence due to the statistical averaging of the gradient can be neglected, and the observed temperature dependence is connected principally with changes in the static gradient due to the thermal broadening.

Comparison of the calculated value of the electric-field gradient for different temperatures in the tetragonal phase, using a pointlike ion model, with the experimental results has shown that the temperature dependence of the NQR frequencies can be well explained when account is taken of the temperature dependence of the lattice parameters and of the ion shifts. Satisfactory

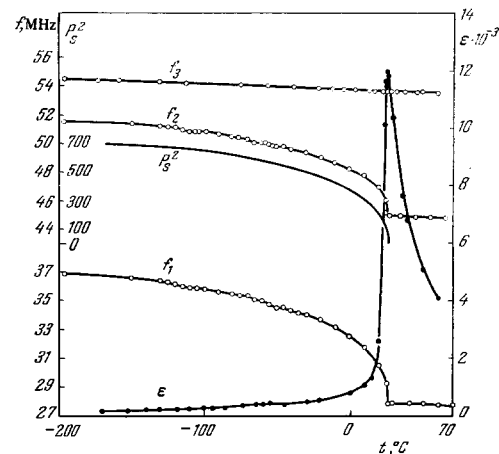


FIG. 7. Temperature dependence of the NQR frequencies  $f_1$ ,  $f_2$ , and  $f_3$ , of the dielectric constant, and of the square of the spontaneous polarization  $P_s^2$  ( $\mu\text{C}^2/\text{cm}^4$ ) in antimony sulfidite [123].  $f_1$  – frequency of  $\text{Sb}^{121}$  ( $3/2 \rightarrow 1/2$ ) transition;  $f_2$  – frequency of  $\text{Sb}^{123}$  ( $3/2 \rightarrow 1/2$ ) transition;  $f_3$  = frequency of  $\text{Sb}^{123}$  ( $5/2 \rightarrow 3/2$ ) transition.



agreement between the calculated and experimental data indicates that the ion model is applicable to  $\text{KNbO}_3$ .

The spin-echo method<sup>[122]</sup> has recently revealed NQR signals and investigated their temperature dependences in crystals of antimony sulfoiodide and sulfo-bromide<sup>[123, 124]</sup> (Fig. 7). The electric-field gradient of antimony sulfoiodide varies like  $P_S^2$  in the vicinity of the Curie temperature, in analogy with the results obtained for barium titanate by the EPR<sup>[69]</sup> and the Mossbauer<sup>[125]</sup> methods. In addition to the anomalies in the temperature dependence of the frequencies at the Curie point, anomalies were observed in the 210–230°K region, and also at 160°K, which apparently correspond to phase transitions.

#### 4. Investigations of Ferroelectrics by the Mossbauer Method

An investigation of the  $\gamma$ -ray resonance-absorption spectra in the Mossbauer effect can yield interesting information concerning the dynamics of the crystal lattice, the gradients of the electric fields, the character of the chemical bond, etc.

As predicted theoretically,<sup>[126]</sup> the probability of the Mossbauer effect in the ferroelectric Curie point should decrease as a result of the possible excitation of low-energy phonons corresponding to the soft "ferroelectrically-active" oscillation mode. This was indeed confirmed by experiment.

The temperature dependence of the Mossbauer effect in  $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{N}_3$  solid solutions enriched with the isotope  $\text{Sn}^{119}$  was investigated in<sup>[127-129]</sup>. It was shown that the probability of the Mossbauer effect actually goes through a minimum at the Curie point (Fig. 8). It turned out also that in solid solutions with sufficiently large  $\text{BaSnO}_3$  content the minimum of the Mossbauer effect lies at a lower temperature than the maximum of the dielectric constant. This was attributed to the fact that at these concentrations of the solid solution the phase transition becomes smeared out and the Curie temperature of the microscopic regions enriched with Sn is lower than the average Curie temperature of the solid solution.

The minimum of the probability of the Mossbauer effect at the Curie point was observed also on  $\text{Fe}^{57}$  nuclei in  $\text{BaTiO}_3$ <sup>[125]</sup> and in  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ .<sup>[130]</sup> Thus, investigations of the Mossbauer effect also confirm the correctness of the concepts of the dynamic theory of

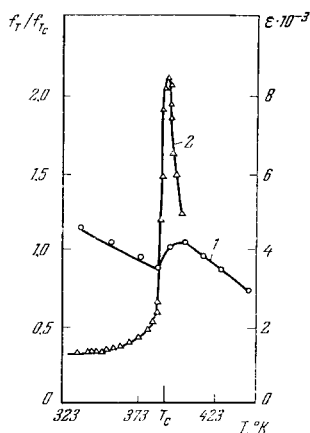


FIG. 8. Temperature dependence of the probability of the Mossbauer effect (curve 1) and of the dielectric constant (curve 2) in  $\text{Ba}(\text{Ti}_{0.99}\text{Sn}_{0.01})\text{O}_3$  (from [128]).

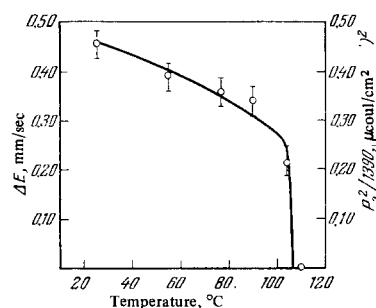


FIG. 9. Temperature dependences of the quadrupole splitting  $\Delta E$  (experimental point) and of the square of the spontaneous polarization in  $\text{BaTiO}_3$  (from [125]).

ferroelectricity. It should be noted, however, that the minimum of the Mossbauer effect on  $\text{Sn}^{119}$  at the Curie point was not observed in some investigations (see, for example, [131]).

In the ferroelectric phase, the resonance line splits into two components as a result of the quadrupole interaction. The quadrupole splitting turned out to be of the same order in  $\text{BaTiO}_3$  and its solid solutions in  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ .<sup>[125, 127-130]</sup>

Figure 9 shows the temperature dependences of the quadrupole splitting  $\Delta E$  and of the square of the spontaneous polarization in  $\text{BaTiO}_3$ . The good agreement between these relations shows that in the tetragonal phase of  $\text{BaTiO}_3$  the electric field gradient (which is directly proportional to the quadrupole splitting) is proportional to the square of the spontaneous polarization, in good agreement with the results of other investigations of ferroelectrics of the displacement type. In addition, a jump of the isomer shift at the Curie point was observed in [125] and was attributed to the change of the degree of covalence of the chemical bond when spontaneous polarization sets in.

In the investigation of the Mossbauer effect on  $\text{BaTiO}_3$  crystals treated by various methods,<sup>[125, 132]</sup> a change was observed in the surrounding of the  $\text{Fe}^{57}$  impurity, depending on the heat treatment of the crystal. In many cases, the  $\text{Fe}^{57}$  impurity formed complexes with the compensating oxygen vacancies, and under certain conditions a vacancy of the axial type occurred. Thermal quenching from a high temperature has made it possible to obtain a more perfect local surrounding of  $\text{Fe}^{57}$ , making it possible to measure the quadrupole splitting connected with the occurrence of the spontaneous polarization.

#### VI. DIELECTRIC PROPERTIES IN THE MICROWAVE REGION

The dielectric properties of ferroelectrics have been the subject of many investigations, a large part of which has been systematized, for example, in [9-13]. We shall therefore deal mainly with investigations of a number of ferroelectrics in the microwave region, to which much attention has been paid recently. Let us consider the most characteristic features of the frequency dependence of the dielectric constant and losses in ferroelectrics with phase transitions of the displacement type and phase transitions of the order-disorder type.

The most detailed investigations were those of the

dispersion of  $\epsilon$  in barium titanate (phase transition of the displacement type).

In the paraelectric phase, both in single-crystal and polycrystalline barium titanate, the dielectric constant is independent of the frequency up to the frequencies of the natural oscillations of the crystal lattice,<sup>[133-139]</sup> the lowest of which lies in the millimeter band (see Ch. IV). According to the latest data,<sup>[136]</sup> the dispersion of  $\epsilon$  comes into play at frequencies above  $\sim 5 \times 10^{10}$  Hz.

In the ferroelectric phase of single-domain barium titanate crystals, dispersion appears as a result of the "clamping" of the piezoelectric oscillations, whose frequencies, for crystals of ordinary dimensions, lie in the region up to  $10^7$  Hz. Owing to the piezoelectric clamping,  $\epsilon$  drops to approximately half its value. With further increase of the frequency, the dielectric constant of single-domain crystals remains unchanged, just as in the paraelectric region, up to the natural frequencies of the lattice vibrations. For example, the value  $\epsilon_a \sim 2000$  is maintained in the direction perpendicular to the spontaneous polarization.<sup>[133, 146]</sup>

In multidomain crystals and in ceramics, there is observed low-frequency dispersion (up to frequencies  $\sim 10^5$  Hz) attributed to relaxation of the orientational domain polarization, which causes a lowering of  $\epsilon$  by 10-20% in weak fields.<sup>[140, 141]</sup> In strong fields, such a dispersion was observed in<sup>[142, 143]</sup>. In the  $10^8$ - $10^{10}$  Hz region, an appreciable dispersion of the dielectric constant, called microwave dispersion of the ferroelectrics, is observed (see, for example, <sup>[136, 144-146]</sup> and Fig. 10). This dispersion is connected with the domain structure, as is indirectly evidenced, for example, by the absence of such dispersion in antiferroelectrics with the perovskite structure.<sup>[147-150]</sup> The nature of this dispersion is not yet fully clear. Many authors connected with the inertia of the domain-boundary motion.<sup>[151, 152]</sup> In<sup>[153]</sup> is proposed a model of individual vibration steps on  $180^\circ$  domain boundaries, the widths of which are determined by the distance between the points of pinning of the domain boundary on the impurities. The dimensions of these steps are smaller than the critical dimensions of the domain nuclei capable of growing in weak fields. An analysis of the oscillations of the local regions of the domain boundaries makes it possible to overcome the known difficulty of the theory of domain-boundary motion,<sup>[151]</sup> connected with the fact that the motion of the boundary as a whole calls for too large a thermal

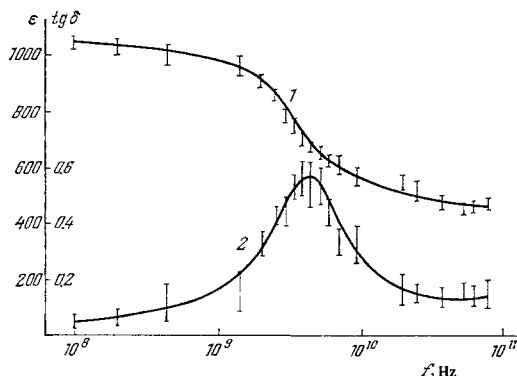


FIG. 10. Frequency dependence of  $\epsilon$  (curve 1) and of  $\tan \delta$  (curve 2) of polycrystalline barium titanate at room temperature (from <sup>[145]</sup>).

activation energy.<sup>[154]</sup> A number of authors attribute the microwave dispersion of ferroelectrics to the Devonshire mechanism, which is connected with the clamping of the piezoelectric oscillations of the individual domains.<sup>[155, 156]</sup> It has not yet been possible to separate these two possible contributions to the microwave dispersion. However, the shift of the dispersion region towards lower frequencies in the so-called ferroelectrics of complex composition (Fig. 11), in which the dimensions of the domains are smaller than in barium titanate, and consequently the piezoresonance frequencies should be higher, apparently offers evidence that the inertia of the domain-wall motion makes an appreciable contribution to the microwave dispersion.<sup>[157-159]</sup> As seen from Fig. 11, in the compound  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ , which has a smeared-out phase transition, the maximum of  $\epsilon$  shifts with increasing measurement frequency towards the region of higher temperatures. In other words, relaxation polarization is observed in the region of the ferroelectric phase transition. In the decimeter wavelength band, the shift of the maximum  $\epsilon$  stops.<sup>[157]</sup> The relaxation character of the polarization, according to <sup>[160, 166]</sup>, can be connected with the motion of the domain boundaries and the boundaries between the ferroelectric and paraelectric phases. The halt in the shift of the maximum of  $\epsilon$  in<sup>[157]</sup> is attributed to the fact that there is no longer a ferroelectric phase in that temperature region, in which this maximum should have been observed in the case of ordinary relaxation polarization. It is possible to explain similarly the dispersion of  $\epsilon$  in solid solutions of barium titanate, in which the phase transition is smeared out and dispersion of  $\epsilon$  is observed above their average Curie temperature (see, for example, <sup>[145]</sup>).

Dispersion of the dielectric constant should be observed in ferroelectrics and antiferroelectrics with ready-made dipole moments in the paraelectric phase. Its frequency should coincide with the relaxation frequencies of these dipole moments.<sup>[162]</sup> Indeed, such a

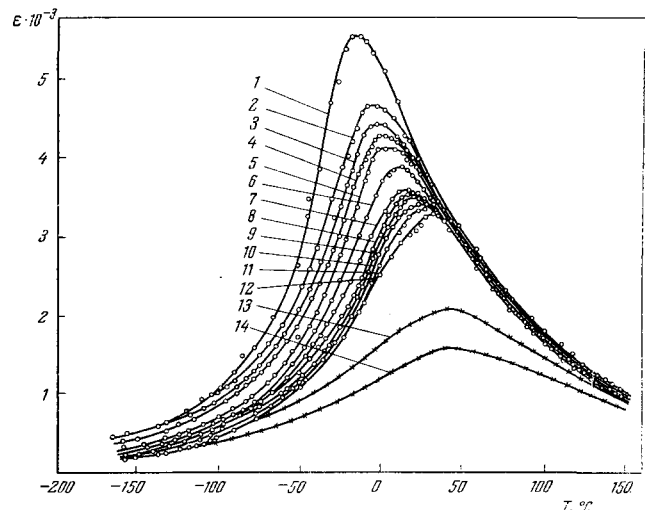


FIG. 11. Temperature dependence of the dielectric constant of the crystal  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  at different frequencies (from <sup>[158]</sup>). 1 - 1 kHz; 2 - 45.6 kHz; 3 - 139 kHz; 4 - 445 kHz; 5 - 4.41 MHz; 6 - 4.42 MHz; 7 - 13 MHz; 8 - 25 MHz; 9 - 34 MHz; 10 - 40 MHz; 11 - 44 MHz; 12 - 50 MHz; 13 - 1500 MHz; 14 - 2000 MHz.

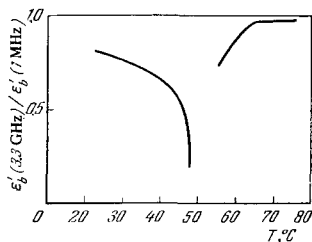


FIG. 12. Temperature dependence of the ratio of  $\epsilon$  at 3.3 GHz to  $\epsilon$  at 1 MHz in sodium nitrite (from [163]).

relaxation-type dispersion was observed in a number of ferroelectrics of this type. Figure 12 shows the temperature dependence of the ratio of  $\epsilon$  at 3.3 GHz to  $\epsilon$  at 1 MHz in sodium nitrite according to [163]. According to [164], an asymmetrical minimum of  $\epsilon'$  is observed in the region of the Curie temperature at high frequencies. In the paraelectric phase,  $\epsilon$  of sodium nitrite obeys the Debye formula with one relaxation time. [164] The dielectric dispersion in this compound is apparently connected with the relaxation of the  $\text{NO}_2^-$  dipole groups, which can rotate at high temperatures around the  $a$  axis (see Ch. IV). Generally speaking, however, more complicated cases are also possible, when a set of relaxation times is observed, and the distribution of the relaxation times varies with the temperature. According to [165], the dielectric constant of Rochelle salt in the paraelectric phase obeys the well-known Cole-Cole formula [166]

$$\epsilon_{\omega} = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + (j\omega\tau_r)^{1-h}}$$

where  $\epsilon_{\omega}$ ,  $\epsilon_{\infty}$ , and  $\epsilon_0$  are the dielectric constants at the measurement frequency  $\omega$ , at infinite frequency, and at zero frequency, while  $\tau_r$  is the relaxation time and  $h$  is a certain parameter,  $0 \leq h \leq 1$ .

When the temperature increases,  $h \rightarrow 0$  and the dielectric constant satisfies the Debye formula. The average relaxation frequency increases from  $3 \times 10^9$  Hz at  $24^\circ\text{C}$  to  $8 \times 10^9$  Hz at  $35^\circ\text{C}$ .

The ferroelectrics of the  $\text{KH}_2\text{PO}_4$  group exhibit the piezoeffect in the paraelectric phase. Consequently, dispersion is observed in them as a result of the clamping of the piezoelectric oscillations. As is well known, the Curie-Weiss temperature of the "clamped" crystal is lower than that of the free crystal, and the Curie-Weiss constants are identical. [167] In [163] they observed relaxation effects at 9.2 GHz in deuterium-substituted  $\text{KH}_2\text{PO}_4$ . It is shown in [168, 169] that the temperature dependence of  $\tan \delta$  in ferroelectrics of this group is similar to the corresponding dependence in strontium titanate, and is well explained from the point of view of the dynamic theory. [29] It turns out that

$$\text{tg } \delta_c = \frac{\alpha + \beta T + \gamma T^2}{T - T_c}$$

Such a behavior of  $\tan \delta$  cannot be explained within the framework of Mason's theory. [162] At the present time it is still unclear what contributions to the mechanism of spontaneous polarization in ferroelectrics of this group are made by ordering of the ready-made dipole moments, by the tunnel effect of the protons, and by the shifts of the ions, and to what degrees the concepts of the dynamic theory are applicable in this case.

In the ferroelectric phase, in the case of an order-disorder transition, there can occur, besides disper-

sion due to the piezoelectric clamping, also dispersion due to various types of relaxation processes. In the case of incomplete order, the "unbound" dipole moments can apparently make a contribution near the Curie temperature. In multidomain crystals, relaxation processes connected with various kinds of domain-boundary motions are possible. At low temperatures, a contribution can be made by the relaxation of the space charges. Thus, for example, in triglycine sulfate at room temperature, two dispersion regions were observed: at  $10^2$ - $10^3$  Hz and at  $10^6$ - $10^7$  Hz. [170-173] These relaxation processes cannot be described by a single relaxation time. The nature of the dispersion in these frequency regions has not yet been thoroughly studied.

Thus, when the frequency drops to  $10^{11}$  Hz, the following main mechanisms contributing to the dispersion of  $\epsilon$  can be observed in ferroelectrics: various kinds of relaxation processes connected with the presence of defects, space charge, etc.; piezoelectric clamping of the crystal or of individual domains; resonant processes connected with motion of polar regions and their boundaries and of domain boundaries (or individual sections of domain boundaries). In ferroelectrics of the order-disorder type, there is added to these mechanisms also the relaxation of the unbound dipole groups, whose frequencies lie in the microwave band near the Curie temperature of the investigated ferroelectrics.

In the  $10^{10}$ - $10^{11}$  Hz frequency region, low-frequency optical modes apparently begin to contribute to the dispersion. This leads to an overall growth of the level of the dielectric losses in this region (which is superimposed on the growth of  $\tan \delta$  as a result of the microwave dispersion in multidomain samples, which was referred to above). This agrees also with the growth of  $\tan \delta$  of antiferroelectrics in this frequency region. [148, 150]

### VII. ELECTROOPTICAL PROPERTIES AND CERTAIN OTHER NONLINEAR OPTICAL PHENOMENA IN FERROELECTRICS

The electrooptical effect is due to the nonlinear dependence of the polarizability of the medium on the electric field intensity. The electrooptical effect in ferroelectrics is discussed, for example, in [174, 175].

The electrooptical effect can be expressed with the aid of equations having the form

$$\Delta a_{ij} = r_{ijk} E_k + R_{ijkl} E_k E_l + \dots \tag{1}$$

where  $\Delta a_{ij} = a_{ij}(E) - a_{ij}(0)$  is the increment of the polarization constants of the substance ( $a = 1/\epsilon = 1/n^2$ , where  $\epsilon$  is the dielectric constant and  $n$  is the refractive index),  $E_k$  and  $E_l$  are the components of the electric field intensity vector,  $r_{ijk}$  are the coefficients of the linear electrooptical effect (components of a third-rank tensor), and  $R_{ijkl}$  are the coefficients of the quadratic electrooptical effect (components of a fourth-rank tensor).

In turn, owing to the presence of elasto-optical effects, the deformation of the crystal in the electrical field (piezoeffect and electrostriction) will influence the polarization constants. Therefore the first term of Eq. (1) can be written in the form

$$r_{ijk}E_k = (r_{ijk}^* + p_{ijlm}d_{klm})E_k, \quad (2)$$

where  $r_{ijk}^*$  are the coefficients of the true electrooptical effect, which is not connected with the inverse piezoeffect,  $p_{ijlm}$  are the components of the elasto-optical coefficient tensor, and  $d_{klm}$  are the piezoelectric coefficients. Similar relations hold for the quadratic electrooptical effect.

The equations of the electrooptical effect can be written in terms of the components of the polarization vector of the crystal instead of the field intensity. We then get an equation of the form

$$\Delta a_{ij} = m_{ijk}P_k + M_{ijkl}P_kP_l, \quad (3)$$

where  $m_{ijk}$  are the linear and  $M_{ijkl}$  the quadratic electrooptical effect, while  $P_k$  are the components of the total polarization of the crystal.

Such an expression for the electrooptical effect is particularly convenient for ferroelectrics, since the influence of the temperature dependence of the dielectric constant, which enters in  $P_j$ , is thereby eliminated.

Therefore the coefficients  $M_{ijkl}$  and  $m_{ijk}$  exhibit in many cases a very weak temperature dependence.

The transition into the ferroelectric state is accompanied by linearization of the quadratic electrooptical effect, similar to the linearization of the electrostriction and to the appearance of the piezoeffect. Indeed, if the birefringence is proportional to the square of the polarization, we have

$$\Delta n = k(P_s + P_{ind})^2 = kP_s^2 + 2kP_sP_{ind} + kP_{ind}^2, \quad (4)$$

where  $P_s$  is the spontaneous polarization and  $P_{ind}$  is the induced polarization.

If  $P_{ind} < P_s$ , a condition satisfied in the ferroelectric phase, we obtain  $\Delta n = A + 2kP_sP_{ind} = A + BP_{ind}$ , where  $A$  and  $B$  are certain constants, i.e., a linear electrooptical effect will be observed, the magnitude of which is proportional to the spontaneous polarization.

Such a linearization gives rise to a linear effect in perovskite-structure ferroelectrics in which only the quadratic effect is observed in the paraelectric phase. If a linear effect is observed in the paraelectric phase, then new components of the linear effect are observed in the ferroelectric state.

The new components  $r_{ij}$  of the tensor of linear coefficients\* are proportional to the product of  $\epsilon$  (more accurately, the induced polarization) by the spontaneous polarization (if higher-order effects are disregarded). The new tensor components  $m_{ij}$ , which appear as a result of linearization of the quadratic effect, will be accordingly proportional to  $P_s$  (see, for example, [176, 177]). The components  $m_{ij}$ , not being the results of linearization, depend little on the temperature.

At the Curie point, a change in the birefringence is observed. The temperature dependence of the birefringence of lithium niobate was recently measured. [176, 179] At room temperature this crystal is optically negative, and at 800–900°C the birefringence passes through zero and then becomes positive, increasing almost all the

way to the Curie temperature. In the region of the Curie temperature, a deceleration of the growth of  $\Delta n$  is observed. [179]

The change of birefringence at the Curie point can be regarded as a spontaneous electrooptical effect that results from the occurrence of spontaneous polarization. Therefore in crystals with perovskite structure, the relation  $\Delta n = \text{const} \cdot P^2$  holds, where  $P$  is the total polarization of the crystal. This relation is satisfied in a certain temperature interval both when external electric fields are applied and in the absence of an external field. [180, 181]

Numerous attempts were made to calculate theoretically the magnitude of the birefringence, resulting from the spontaneous electrooptical effect in  $\text{BaTiO}_3$  and in certain other ferroelectrics. [182–186] The model of point-like polarizable ions was used in this case. The results of these investigations are not in satisfactory agreement with one another and with the experimental data. In the latest investigations, [183–186] a value of  $\Delta n$  close to zero was obtained for barium titanate. According to the available experimental data, barium titanate is an optically negative crystal. [180, 187, 188] This deviation from the experimental data is usually attributed to the need for taking into account the anisotropy of the electronic polarizability of the oxygen ions, which should result from saturation of the polarizability in strong internal fields. The complicated temperature dependence of the birefringence of lead titanate, according to a hypothesis advanced in [184], is also due to the influence of the anisotropy of the polarizability of the oxygen. It must be noted, however, that the calculation performed in [183] for  $\text{BaTiO}_3$  has shown that the dependence of  $\Delta n$  on the deformation of the cell is itself complicated in form. For lead titanate, no complete calculation of the dependence on the cell deformation was made at all. It is possible that in ferroelectrics such as  $\text{KH}_2\text{P}_2\text{O}_7$ , Rochelle salt, or triglycine sulfate the effects of saturation of the optical dielectric constant play a lesser role, owing to the lesser magnitude of the refractive indices and the complicated configuration of the internal field which are not parallel to the resultant polarization. [9]

By way of an example, let us consider in greater detail the electrooptical properties of certain ferroelectrics. In the paraelectric phase of crystals with a perovskite structure (point symmetry group  $m3m$ ) there are three different nonvanishing quadratic electrooptical coefficients  $R_{11}$ ,  $R_{12}$ , and  $R_{44}$ .

With increasing temperature, the magnitude of the electrooptical coefficients  $R_{ij}$  in barium titanate decreases approximately in accordance with the decrease of the dielectric constant. [189] The coefficients  $M_{ij}$ , to the contrary, are practically independent of the temperature and, moreover, for many compounds with perovskite structure ( $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{KTaO}_3$ ,  $\text{KTa}_{0.35}\text{Nb}_{0.65}\text{O}_3$ ) the values of these coefficients are close [190, 191] (Table I). The independence of  $M_{ij}$  of the temperature is due simply to the fact that it enters in the expression for the polarization, in terms of which these coefficients are determined (see Eq. (3)).

The constancy of the coefficients  $M_{ij}$  for most perovskites has made it possible [39] to attempt to esti-

\*We shall use henceforth a two-index notation for the components of the tensors of the electrooptical coefficients.

Table I. Quadratic electric coefficients of certain ferroelectrics with perovskite structure.

Crystal	$R_{ij}, 10^{-8}$ cgs esu	$M_{ij}, 10^{-12}$ cgs esu
BaTiO <sub>3</sub>		$M_{11} - M_{12} = 1.44$ <sup>190</sup> $M_{44} = 1.88$
SrTiO <sub>3</sub>		$M_{11} - M_{12} = 1.55$ <sup>190</sup>
KTaO <sub>3</sub>		$M_{21} - M_{12} = 1.77$ <sup>190</sup> $M_{44} = 1.33$
KTaNb <sub>0.65</sub> O <sub>3</sub> (KTN)		$M_{11} - M_{12} = 1.93$ <sup>190</sup> $M_{11} = 1.5, M_{12} = 0.43, M_{44} = 1.83$
PbMg <sub>1/3</sub> Nb <sub>2/3</sub> O <sub>3</sub>	$R_{11} - R_{12} = 13.1, R_{44} = 23$ $n_0^3 (R_{11} - R_{12}) = 218$ <sup>192</sup>	$M_{11} - M_{12} = 0.183$ <sup>192</sup> $M_{44} = 0.03$
PbZn <sub>1/3</sub> Nb <sub>2/3</sub> O <sub>3</sub>	$n_0^3 (R_{11} - R_{12}) = 290$ <sup>193</sup>	$n_0^3 (M_{11} - M_{12}) = 1.72$ <sup>193</sup>

mate the magnitude of the electrooptical effect by calculating the change of the electron band structure for ionic displacements connected with the polarization (see Ch. IV). This calculation yielded perfectly satisfactory agreement with experiment. The coefficients  $M_{ij}$  increase with decreasing wavelength in a region close to the intrinsic absorption edge, in good agreement with the concepts of dispersion theory.

In [192, 194], and independently in [195], a large electrooptical effect was reported in a ferroelectric with the complex composition PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub> (see Fig. 13 and Table I). Similar results were obtained also for another complex ferroelectric, PbZn<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>. [193] Such large values of the coefficients  $R_{ij}$  are connected in [192] with the singularities of the smeared-out phase transitions. Because of these, the domain orientation and the increase of the volume of the ferromagnetic phase in the electric field contribute to the electrooptical effect in a wide temperature interval.

Figure 14 shows the temperature dependence of the linear coefficient  $r_C \approx r_{33} - r_{31}$  in the tetragonal phase of barium titanate in accordance with [196]. It is seen from Fig. 14 that the character of the temperature dependence corresponds to the temperature dependence of the product of  $\epsilon_C$  by the polarization (see Eq. (4)).

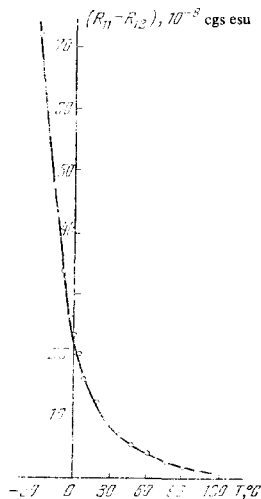
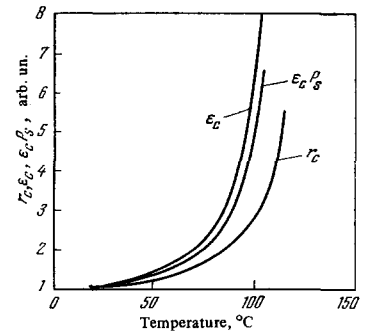


FIG. 13. Temperature dependence of the quadratic electrooptical coefficients  $R_{11} - R_{12}$  in crystalline PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub> (from [192]).

FIG. 14. Temperature dependence of linear electrooptical coefficient  $r = r_{33} - r_{31}$  of tetragonal barium titanate, and a comparison with the temperature dependence of the dielectric constant and of the product of the dielectric constant by the spontaneous polarization (from [196]).



Recently, intensive investigations have been made of the electrooptical properties of triglycine sulfate. [187-203] In [197, 198, 201-203] they investigated only the electrooptical coefficients that determine the deformation of the indicatrix. The temperature dependence of the rotation of the indicatrix, resulting from the thermal optical and spontaneous electrical and elastic effects was studied in [199]. In [200] they investigated the effect of applying a field along the ferroelectric b axis on the orientation of the indicatrix. The linear effect in the ferroelectric phase of TGS, just as in barium titanate, is by its nature a linearized quadratic effect. Therefore the temperature dependence of the coefficients  $r_{ij}$  is determined by the product  $\epsilon P_S$ . In particular, according to [200], the temperature dependence of the coefficient  $r_{52}$  is proportional to  $\epsilon_2 P_S \sim A (T_C - T)^{1/2}$ . The temperature dependence of the linear coefficients  $m_{ij}$  is analogous to the temperature dependence of the polarization. [203]

When an electric field is applied, a linear effect is still observed even 2-3° above the Curie temperature (Fig. 15), and is due to the "smearing" of the first-order phase transition that takes place in TGS in an electric field. [197] At higher temperatures, a quadratic effect is observed. The contribution of the "true" electrooptical effect to the total effect, after subtracting the contribution of the piezooptical effect in TGS, amounted to 90%, thus indicating that the contribution of the electron polarization is decisive. [197]

The investigations of the electrooptical effect were continued in potassium dihydrophosphate and in isomor-

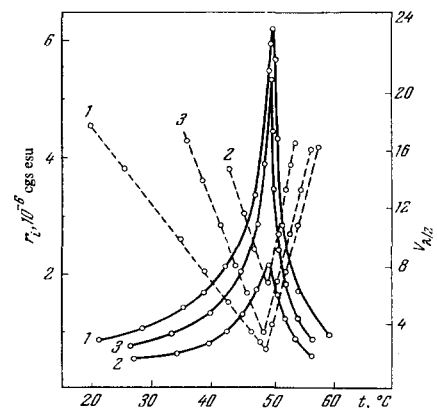


FIG. 15. Temperature dependence of the linear electrooptical coefficients (solid lines) and of the half-wave voltages (in kV; dashed lines) in triglycine sulfate (from [197]).

phic ferroelectrics. Among the latest papers, mention should be made of an investigation<sup>[204]</sup> of the linear effect in KDP and ADP. The spontaneous effect was investigated in<sup>[206]</sup>. Results of an investigation of the quadratic effect are reported in<sup>[208]</sup>. An analysis shows (see, for example,<sup>[207]</sup> that at certain orientations of the electric field and of the light there is no linear effect in KDP, and only the quadratic effect is observed. Details on the results of investigations of electrooptical properties of various ferroelectrics can be found in the review.<sup>[208]</sup>

A number of recent papers report investigations of the electrooptical properties of a number of ferroelectrics with the structure of potassium-tungsten bronze, namely strontium-barium niobates<sup>[209]</sup> and the compounds  $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ ,<sup>[210]</sup>  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ ,<sup>[211]</sup> and  $\text{K}_6\text{Li}_4\text{Nb}_{10}\text{O}_{30}$ .<sup>[212]</sup> These materials have many advantages over previously known electrooptical materials. In particular, the electrooptical coefficients  $r_{ij}$  of  $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ , the homogeneous crystals of which can be obtained relatively easily, are higher by one order of magnitude than those of lithium niobate.<sup>[210]</sup>

Closely related to investigations of the electrooptical properties of ferroelectrics are investigations of the optical activity of ferroelectrics, particularly the reversal of the sign of the optical activity in an electric field. Great interest attaches to the observation, in<sup>[213]</sup>, of a change of the direction of rotation of the polarization plane of light when an electric field is applied to lithium hydroselenite ( $\text{LiH}_3(\text{SeO}_3)_2$ ). In this crystal the direction of rotation has opposite signs for two optical axes, but the absolute strengths of the rotation are equal. The crystal is a uniaxial ferroelectric and breaks up into  $180^\circ$  domains. The optical axes of the domains are parallel. When the crystal polarization is reversed by means of an electric field, the positions of the optical axes are interchanged, and therefore a change in the sign of the rotation of the polarization plane is observed for light propagating along the optical axes.

Figure 16 shows the hysteresis loop of the per-unit rotation of the plane of polarization of light after eliminating the influence of the electrooptical effect, in accordance with the data of<sup>[214]</sup>. The presence of optical activity in this crystal, in the opinion of Pepinski, is due to the Se—O bonds, since the dispersion observed by him in the rotating ability lies in the region of the absorption band of the  $\text{SeO}_2$  ion.<sup>[215, 216]</sup>

A crystallographic analysis of the possibility of changing the sign and magnitude of the optical activity by electric and mechanical polarization of ferroelectrics of various classes is presented in<sup>[217]</sup>. The optical activity and the change of sign are possible in enantiomorphic classes 1, 2, 3, 4, and 6, and in the planal classes  $m$  and  $2mm$ .

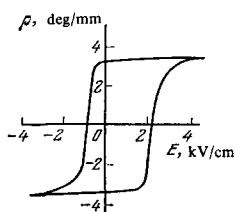


FIG. 16. Hysteresis loop of per-unit rotation of the plane of polarization of light for crystalline lithium-hydroselenite at room temperature (from<sup>[214]</sup>).

The development of nonlinear optics was greatly accelerated by the development of lasers by N. G. Basov, A. M. Prokhorov, and C. Townes. This exerted a strong influence on the intensification of electrooptical research. Whereas earlier, in the analysis of electrooptical phenomena, it could be assumed that the electron polarization of the medium does not depend on the intensity of the light-wave field, when laser sources are used the nonlinearity of the medium with respect to the light wave must be taken into account, since the intensity of the light-wave field becomes comparable with the internal fields in the medium. The analysis and the conditions for obtaining various nonlinear effects can be found, for example, in<sup>[218-220]</sup>.

To obtain large nonlinear effects it is necessary, besides having a medium with large nonlinearity, also to satisfy the synchronism conditions, according to which a constant phase relation must be maintained throughout in the propagating waves. For the case of three interacting waves, they have, for example, the following form:

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3$$

( $\mathbf{k}$ —wave vectors of the interacting waves). When this condition is satisfied, accumulation of the energy of the waves of the resultant harmonics will take place as they propagate through an infinite crystal. If the medium is bounded (for example, the sample has a length  $l$ ), then accumulating interaction is possible also at not too large deviations from the synchronism condition  $\Delta = \mathbf{k}_3 - \mathbf{k}_1 - \mathbf{k}_2 \neq 0$ . The length of the sample at which energy accumulation is still possible (the length of coherent interaction) is determined by relation of the type  $l\Delta \approx \pi/2$ . When  $\Delta \rightarrow 0$  we have  $l \rightarrow \infty$ . The nonlinearity of the crystal can be characterized with the aid of the value of the resultant polarization of the second kind, i.e., that part of the dielectric polarization, which varies with double the frequency compared with the frequency of the incident laser beam (or second-harmonic polarization). In this case the following relation is satisfied

$$P_{2i} = d_{ijl} E_j E_l; \quad (5)$$

$P_{2i}$  are the polarization second-harmonic components;  $E_j$  and  $E_l$  are the components of the symmetrical tensor  $\mathbf{EE}$ , made up of the components of the field intensity of the incident wave;  $d_{ijl}$  are the components of the nonlinearity-coefficient tensor.

According to<sup>[221]</sup>, the number of independent components of this third-rank tensor, in an approximate analysis and neglecting dispersion and losses, can be assumed to equal 10. It has been shown by now that the assumption of<sup>[221]</sup> is valid with sufficiently high accuracy for all the investigated crystals.<sup>[222]</sup> Second harmonic generation and the linear electrooptical effect should be connected with each other.<sup>[229]</sup> In the simplest case, the relation between them should be of the type

$$r_{ijl} = -4\pi A d_{ijl}, \quad (6)$$

where  $r_{ijl}$  is the linear electrooptical coefficient,  $d_{ijl}$  is the nonlinearity coefficient, and  $A$  is the square of the polarization constant ( $1/\epsilon\epsilon$ ). However, relations of

this kind are usually not satisfied in experiments, apparently owing to the differences in the experimental conditions: when the electrooptical effect is measured, the frequency of the applied electric field is lower than the natural frequencies of the lattice vibrations, and the ionic polarization plays a sufficiently significant role; in the measurements of the nonlinearity coefficients, the electric field varies at the optical frequency, which lies higher than the natural frequencies of the lattice vibrations. In any case, it can be stated that the larger the electrooptical effect due to the electron polarization, the larger, generally speaking, the optical linearity of the crystal.

The most effective crystals used in nonlinear optics are crystals of the ferroelectric and antiferroelectric groups of  $\text{KH}_2\text{PO}_4$  and  $\text{LiNbO}_3$  (see, for example, [223, 208]). In these crystals it is possible to satisfy the synchronism conditions, owing to a fortunate relation between the refractive indices of the ordinary and extraordinary waves of the different harmonics. For example, in crystals of the  $\text{KH}_2\text{PO}_4$  group, which are uniaxial optically-negative crystals in the tetragonal phase, the relations  $n_1^0 > n_1^e$  are satisfied, and even  $n_1^0 > n_2^e$  and  $n_1^0 > n_3^e$  ( $n_1^0$ —refractive index of the ordinary wave of the initial frequency,  $n_1^e$ —that of the extraordinary wave at the initial frequency,  $n_2^e$ —of the extraordinary wave of the second harmonic, etc.). This makes it possible to satisfy, in certain definite crystallographic directions (making an angle  $\theta_0$  with the optical axis, called the synchronism angle) the synchronism conditions. These conditions take, for example, the form

$$k_1^0 + k_1^e = k_2^e \quad \text{or} \quad k_1^0 + k_1^e = k_3^e.$$

A similar situation occurs also in the uniaxial optically negative lithium niobate crystals. The temperature dependence of the nonlinear coefficient  $d_{33}$  and of the coherence wavelength  $l_{33}$  of lithium niobate crystals was investigated in [224].

In addition, noncritical generation of the second harmonic (satisfaction of the synchronism condition for a synchronism angle  $\theta_0 = 90^\circ$ ) is possible in crystals of these groups. No birefringence occurs in this case, and the coherence length of the sample, in which energy accumulation is possible during the generation of the second harmonic, is determined only by the divergence of the laser beam.

For lithium niobate, the condition of noncritical generation of the second harmonic

$$n_1^0 - n_2^e = (n_0^0 - n_2^e) - (n_2^e - n_1^0) = 0$$

can be satisfied at certain definite values of the initial wavelength and the temperature. [225] In [226] they calculated the temperatures for which it is possible to obtain summary frequencies of different lasers under conditions of noncritical phase matching, and also to obtain frequencies half as large as the initial frequency.

The feasibility of noncritical second-harmonic generation in  $\text{RbH}_2\text{AsO}_4$  was demonstrated in [227]. In the case of  $\text{KH}_2\text{PO}_4$ , noncritical second-harmonic generation, according to [228], can be realized near the Curie temperature as a result of a change of the dispersion characteristics with the aid of an electric field. The parameters of the nonlinear materials are discussed in the reviews. [208, 223].

New data continue to appear concerning the nonlinear properties of new crystals. A recent communication reports generation of coherent light emission using a new ferroelectric  $\text{Gd}_2(\text{MoO}_4)_3$ , containing  $\text{Nd}^{3+}$  as an impurity. [229] It is reported in [209-212] that a number of new ferroelectrics with the tetragonal potassium-tungsten bronze structure, with filled cation positions in the lattice, apparently acquire more stable refractive indices when exposed to high-power light than lithium niobate; this pertains to  $\text{K}_6\text{Li}_4\text{Nb}_{10}\text{O}_{30}$  crystals with filled cation positions in triangular channels [212] and also to the crystals  $\text{K}_2\text{Sr}_4\text{Nb}_{10}\text{O}_{30}$  [210] and  $\text{Na}_2\text{Ba}_4\text{Nb}_{10}\text{O}_{30}$ . [211]

### VIII. EXCITATION AND ATTENUATION OF COHERENT PHONONS. HYPERSOUND

In recent years, physicists have found new ways of investigating phonon spectra and anharmonicity of the interaction forces in crystals, by using excitation of coherent phonons, whose frequency reaches  $10^{10}$ – $10^{11}$  Hz. The methods for exciting high-frequency coherent phonons are particularly effective when ferroelectrics are used. It is shown in [230-233] that lithium niobate and tantalate crystals have a high coefficient of conversion of electromagnetic oscillations into elastic oscillations, with very low loss of energy of the propagating elastic waves in the microwave band. The elastic waves are excited in such crystals with the aid of the piezoeffect by the Baranskiĭ method, [234] by placing one of the ends of the sample in the antinode of the electric microwave field. The electromechanical-coupling coefficient for lithium niobate reach 70% in the microwave range. [235] The damping of hypersound is well described on the basis of the theory of Akhiezer. [236 237] for the case  $\omega\tau \ll 1$ , where  $\omega$  is the angle of frequency of the elastic waves and  $\tau$  is the relaxation time of the thermal phonons. As shown by estimates (see, for example, [233]), this condition is satisfied at sufficiently high temperature, including room temperature.

The volume deformation  $\Delta V/V$  produced by the hypersonic wave leads to a frequency change  $\Delta\nu/\nu$  of the thermal phonons ( $\Delta V/V = -\gamma\Delta\nu/\nu$ , where  $\gamma$  is the Gruneisen constant, and consequently to violation of their equilibrium distribution. Restoration of the equilibrium occurs with a lag (phase shift) relative to the stresses

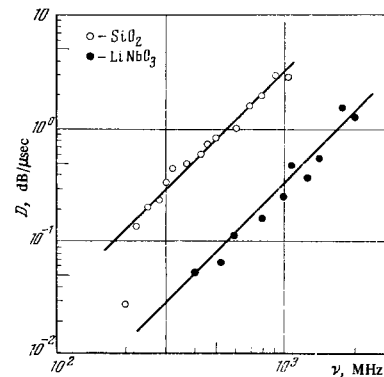


FIG. 17. Dependence of the attenuation of hypersound on the frequency for single-domain lithium-niobate crystal and for X-cut quartz (from [233]).

in the hypersonic wave, thus causing the hypersound energy to be absorbed. Calculation shows that the attenuation is

$$D = 8.686 \frac{\gamma^2 \alpha^2 T \kappa}{\rho v^5} \text{ (dB/cm)},$$

where  $T$ —temperature,  $\kappa$ —thermal conductivity,  $\gamma$ —average Gruneisen constant,  $v$ —average speed of sound ( $3/v^3 = 1/v_l^3 + 2/v_t^3$ ,  $v_l$  and  $v_t$  are the velocities of the longitudinal and transverse waves).

We present some data on the propagation of longitudinal elastic waves in lithium-niobate crystals in the frequency range 200–2000 MHz, as given in [233]. An electric field applied parallel to the sample axis, which coincided with a three-fold symmetry axis, excited longitudinal elastic oscillations. As the result of many reflections from the ends of the sample, a series of pulses was observed, whose amplitude gradually decreased as a result of the losses occurring as the elastic waves propagated through the crystal. Figure 17 shows the experimental data demonstrating the dependence of the attenuation on the frequency in single-domain lithium-niobate crystal and in X-cut quartz. The loss in quartz exceeds the loss in the lithium-niobate crystal by one order of magnitude. As seen from Fig. 17, where the straight lines were drawn assuming a quadratic dependence on the frequency, the hypersound absorption agrees well with theory. [236, 237] The lithium niobate crystals have a relatively high coefficient of conversion of the electromechanical oscillations into elastic oscillations, and are characterized by low elastic micro-wave propagation losses. Obviously, these crystals can be used as passive delay lines for microwave signals.

## IX. NEW TYPES OF FERROELECTRICS

Much attention has been paid recently to the study of crystals exhibiting simultaneously several important properties or phenomena, such as the occurrence of spontaneous polarization in semiconductors with pronounced photoconductivity, or simultaneous occurrence of spontaneous polarization and spontaneous magnetization. This relates also to the possible coexistence of ferroelectricity and superconductivity. In crystals of this kind one should expect new phenomena, a mutual influence of the magnetic and electric subsystems in ferroelectric ferromagnets, an influence of illumination on the ferroelectric properties of crystals with photoconductivity, and many others.

In this chapter we consider the behavior of ferroelectrics of two types.

### 1. Semiconducting Ferroelectrics

Many ferroelectrics, primarily oxide ferroelectrics, are also semiconductors but, as a rule, have a broad forbidden band (usually several electron volts), a low carrier mobility, and an insignificant photoeffect. To be sure, it is possible to make their conductivity high by introducing impurities or by annealing in a reducing atmosphere. We shall consider here semiconducting ferroelectrics and paraelectrics with a pronounced photoeffect (chalcogen-halides of antimony and bismuth) and semiconductors of the IV–VI type (GeTe and SnTe, and also SrTiO<sub>3</sub>) with sufficiently high carrier density.

a) In ferroelectrics of the antimony sulfoiodide group, an electric field causes the absorption edge (the width of the forbidden band) to shift towards shorter wavelengths. [238, 239] Below the Curie temperature the shift is linear in the applied field, but above the Curie temperature it is quadratic. This effect is apparently connected with piezoelectric deformation and with electrostriction in the electric field. [240, 241]

A study of the temperature dependence of the intrinsic absorption edge in these crystals has shown that at the Curie point a jump takes place of the intrinsic-absorption edge [242–245] (Fig. 18). In addition, a change takes place in the coefficient of the temperature dependence of the width of the forbidden band. This jump of the intrinsic absorption edge at the Curie point can be explained on the basis of a thermodynamic analysis [246] (see also [38]).

Indeed, at a relatively high concentration of the nonequilibrium carriers it is necessary to take into account in the expansion of the free energy of the crystal in terms of the parameter  $P$  (polarization) the change of the free energy of the electron subsystem at the phase-transition point. In [246] this is taken into account by including in the expansion a term  $nE_g$ , where  $n$  is the concentration of the nonequilibrium carriers and  $E_g$  is the width of the forbidden band. Then the expansion of the free energy  $F$ , without allowance for the anisotropy and the stresses, takes the form

$$F = F_0 + \alpha P^2 + \frac{\beta}{2} P^4 + \dots + nE_g(P), \quad (7)$$

where  $\alpha(p, T)$  and  $\beta(p, T)$  are the coefficients in the Landau–Ginzburg expansion.

We assume next that the following relation holds:

$$E_g \approx E_{g0} + aP^2, \quad (8)$$

where  $a$  is a certain constant coefficient.

Equation (8) is then substituted in (7), the minimum of the free energy is found, and for second-order phase transitions the jump of the temperature coefficient of the forbidden-band width turns out to be

$$\Delta \left( \frac{E_g}{\partial T} \right)_p = a \frac{\Delta c_{\Theta}}{\Theta \alpha_{\Theta}}. \quad (9)$$

Here  $\Delta c_{\Theta}$  is the jump of the specific heat at the transition point,  $\Theta$  is the Curie temperature in the absence of nonequilibrium carriers, and  $\alpha_{\Theta}$  is a quantity equal to the reciprocal of the Curie constant.

In the case of a second-order phase transition close to the critical Curie point, the coefficients  $(\partial E_g / \partial T)_p$  and  $(\partial E_g / \partial p)_T$  approach infinity, and the signs of these

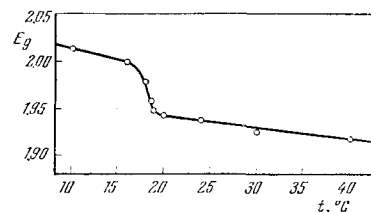


FIG. 18. Temperature dependence of the width of the forbidden band  $E_g$  of SbSI (from [244]).



coefficients are determined by the sign of the constant  $a$ .

In SbSi, the phase transition is close to the critical point, and this explains the large values of  $\partial E_g/\partial T$  and  $\partial E_g/\partial p$ . Their sign corresponds to a positive sign of  $a$ .

Another interesting result of [246] is the predicted shift of the Curie temperature with increasing number of non-equilibrium carriers, as a result of illumination of the crystal. The estimate in [246] shows that the Curie temperature should decrease upon illumination, as in indeed observed in the experiments. [247]

b) An investigation of the inelastic scattering of neutrons has revealed [248] that in a semiconductor with a narrow forbidden band, of the IV-VI type with NaCl structure, namely in an SnTe crystal, there is a transverse optical oscillation with a small vector  $\mathbf{q}$ , whose frequency decreases on approaching 0°K, but, just as in SrTiO<sub>3</sub>, it does not vanish. SnTe forms solid solutions with GeTe. According to [249, 250], a phase transition accompanied by displacements of the ions from the centrally-symmetrical positions is observed in GeTe at 670°K. The temperature of this transition decreases with increasing SnTe content, and tends to 0°K. On this basis it is proposed in [248] that GeTe is a ferroelectric below 670°K. This point of view needs verification.

It is proposed in [251] that the phase transition in the well known metallic superconductor V<sub>3</sub>Si at 27°K (the temperature of transition to the superconducting state is 17°K) is also connected with the existence of a low-frequency branch of optical oscillations and in this sense it is ferroelectric.

In general, the existence of superconductivity in crystals in which there is a low-frequency branch of optical oscillations with a small wave vector  $\mathbf{q}$  is apparently not an accident. In [252-254] are considered the conditions for the occurrence of superconductivity in semiconductors, and it is shown that contributing to the occurrence of superconductivity are the large dielectric constant, the high carrier density, their large effective mass, and some other factors. Consequently, one can expect that certain substances with high dielectric constant will go over into the superconducting state when high carrier density is produced. Indeed, it was demonstrated in [255] that superconductivity is produced in reduced strontium titanate, and the temperature of transition to the superconducting state goes through a maximum as a function of the carrier density. [256] In [257] it is shown that in solid solutions of SrTiO<sub>3</sub> with small contents of BaTiO<sub>3</sub> and CaTiO<sub>3</sub> the superconductivity is produced at somewhat higher temperatures than in SrTiO<sub>3</sub> (the maximum temperature with 6% BaTiO<sub>3</sub> is 0.5°K). The possible occurrence of Cooper pairs at large  $\epsilon$ , even at quasi-free-electron densities lower than in metals, is connected with the decrease of the repelling Coulomb interaction between electrons.

Thus, it can be regarded as proved that a superconducting state is produced in the paraelectric phase of certain crystals. However, the possibility of coexistence of ferroelectricity in superconductivity is not clear, since, on the one hand,  $\epsilon$  decreases on going over to the ferroelectric state, and on the other hand it is not clear how the transition to the superconducting state will affect the conditions for the occurrence of spontaneous polarization.

In concluding this section, we wish to note that the interesting question of the screening action of the carriers on the dipole-dipole interaction, responsible for the occurrence of spontaneous polarization, has not been considered.

## 2. Ferroelectric Ferromagnets

The possibility in principle of obtaining crystals in which magnetic and electric ordering is simultaneously produced was demonstrated first in [258-260] with perovskite-structure crystals as an example. Hexagonal ferroelectric-antiferromagnets were then discovered [261-264] as well as a group of ferroelectric boracites-antiferromagnets and weak ferromagnets. [265-269]

The thermodynamic theory of these substances was developed in [270-273]. The main idea of this theory is to take into account the mixed terms in the thermodynamic potential. This is equivalent to introducing an electro-magnetic susceptibility

$$\chi_{em} = - \frac{\partial^2 \Phi}{\partial H \partial E} \sim (T - T_c)^{-1/2}$$

near the Curie point; here  $H$  is the magnetic field intensity and  $E$  the electric field intensity. From this we get

$$\mathbf{M} = \chi_m \mathbf{H} + \chi_{me} \mathbf{E}, \quad \mathbf{P} = \chi_e \mathbf{E} + \chi_{em} \mathbf{H},$$

where  $\mathbf{M}$  is the magnetization and  $\mathbf{P}$  the polarization.

Thus, the mutual influence of the electric and magnetic subsystems, including the magnetoelectric effect, has been predicted. In addition, it was shown that the susceptibility experiences a positive jump on going over to the ferroelectric-ferromagnetic state. The symmetry of ferroelectric ferromagnets was investigated theoretically in [274, 275].

The first ferroelectric antiferromagnets were the compounds PbFe<sub>1/2</sub>Nb<sub>1/2</sub>O<sub>3</sub> and PbFe<sub>2/3</sub>W<sub>1/3</sub>O<sub>3</sub>. [258-260] Neutron diffraction investigations [276, 277] have shown that the magnetic ordering is of G-type. The temperatures of the magnetic and electric ordering of certain compounds are listed in Table II.

A number of other ferroelectric ferromagnets with perovskite structure were investigated later (see, for example, [288, 289]), including ferroelectric ferrimagnets. [290, 291] The idea of producing ferroelectric ferrimagnets consists in obtaining ferroelectric and simultaneously antiferromagnetic compounds with two or more nonequivalent crystallographic sublattices, containing an unequal number of magnetic ions. This gives rise to an uncompensated antiferromagnetism (ferromagnetism).

Hexagonal manganites have a general form AMnO<sub>3</sub>, where A are ions of Y, Sc, and rare-earths starting with Ho and going to the end of the series (towards ions with smaller radius [261-264]). These compounds are pure antiferromagnets [292-294] and, in addition, are characterized by very high electric-ordering temperatures (~800-900° C). [295, 287, 296] This magnetic structure is described in [297-299].

Investigations [265-269] have led to the discovery and investigation of a number of crystals with borosite structure, revealing simultaneously ferroelectricity and weak ferromagnetism. Their general formula is

Table II. Certain ferroelectric ferromagnets.

Chemical formula	Type of electric and magnetic ordering	Structure	Magnetic transition point, °K	Electric transition point, °K
$\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3$	Ferroelectric antiferromagnet	Perovskite, pseudocubic	363 <sup>258-260</sup>	178 <sup>258-260</sup>
$\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$	Ditto	Ditto	143 <sup>258-260</sup>	387 <sup>258-260</sup>
$\text{PbCo}_{1/2}\text{W}_{1/2}\text{O}_3$	Weak ferromagnetic ferroelectric, becomes antiferroelectric at $65 < T < 305^\circ \text{K}$	» »	9 <sup>278</sup>	65° (ferroelectric) [279], 305° (antiferroelectric) [280]
$\text{BiFeO}_3$	Antiferroelectric, antiferromagnetic	Perovskite, rhombohedral	643 <sup>281-283</sup>	1120 <sup>284-285</sup>
$\text{YMnO}_3$	Ferroelectric, antiferromagnetic	Hexagonal	76 <sup>286</sup>	930 <sup>287</sup>
$\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$	Ferroelectric, weak ferromagnetic	Rhombic	120 <sup>288</sup>	64 <sup>288</sup>

$\text{Me}_3\text{B}_7\text{O}_{13}\text{X}$ , where  $\text{Me} = \text{Cr, Mn, Fe, Co, Ni}$ , and  $\text{X} = \text{Cl, Br, I}$ . The most interesting properties are possessed by  $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ , which reveals weak ferromagnetism in the ferroelectric phase ( $T_C = 64^\circ \text{C}$ ). The spontaneous polarization is directed along the pseudocubic direction  $[001]$ , and the spontaneous magnetization along  $[110]$  or  $[1\bar{1}0]$ , i.e.,  $\mathbf{P}_S \perp \mathbf{M}_S$ . The direction of  $\mathbf{M}_S$  can be changed by an electric field:<sup>[286]</sup> the change of the direction of  $\mathbf{P}_S$  from  $[001]$  to  $[00\bar{1}]$  leads to rotation of  $\mathbf{M}_S$  by  $90^\circ$  from  $[110]$  to  $[1\bar{1}0]$ . Conversely, rotation of the magnetic field from  $[110]$  to  $[1\bar{1}0]$  leads to rotation of  $\mathbf{P}_S$  from  $[001]$  to  $[00\bar{1}]$ . In addition to this effect, which is connected with reversal of polarization, a linear magnetoelectric effect is observed with a susceptibility  $\sim 3.3 \times 10^{-4}$  at  $15^\circ \text{K}$ . Boracites are so far the only ferroelectric ferromagnets in which the mutual influence of the electric and magnetic subsystems has been reliably demonstrated.

A more detailed review of work on ferroelectric ferromagnetic can be found in [300-302].

## X. CONCLUSION

Thus, it can be stated that ferroelectricity is a rapidly developing branch of solid-state physics. The physics of ferroelectric phenomena was produced principally during the last 20 or more years. Numerous classes of ferroelectrics have been discovered, with different crystal structures and with different chemical compositions. A thermodynamic theory has been developed; the foundations of the dynamic theory have been laid; numerous investigations of the dielectric, elastic, thermal, optical, and other properties of various ferroelectrics and antiferroelectrics have been performed. The ferroelectrics have found use in many branches of engineering.

Research on ferroelectric phenomena must still solve the following important problems: 1) The development of a quantum-mechanical theory of ferroelectrics and antiferroelectrics of various types, in which account is taken of anharmonic effects, and comparison of the theory with experiment in a wide range of frequencies and

temperatures. 2) Investigation of the structure of the energy spectra and interaction forces in ferroelectrics by optical, radio spectroscopic, x-ray structure, neutron diffraction, and other methods. 3) Theoretical and experimental investigations of phase transitions due to both long-range and short-range forces, including an investigation of the kinetics of the phase transitions. 4) Investigation of the coexistence of ferroelectricity and ferromagnetism and of the possibility of coexistence of ferroelectricity and superconductivity; observation of the interaction between the magnetic and electric subsystems. 5) Investigation of the influence of carrier screening on the dipole-dipole interaction; investigation of semiconducting ferroelectrics with narrow forbidden bands; investigation of the possible occurrence of ferroelectricity in metals. 6) Study of the conditions for the excitation and damping of hypersound in a wide range of frequencies and temperatures, investigation of nonlinear effects, including parametric excitation, study of the interaction of various branches of the spectrum (optical and acoustic), investigation of the diffraction of light by coherent phonons. 7) Investigation of the influence of the Jahn-Teller effect on the condition for the occurrence of ferroelectricity. 8) Creation of new effective materials for radio electronics, hydroacoustics, computing devices, quantum electronics, and other branches of engineering, particularly the creation of active materials for lasers with a frequency that can be tuned with the aid of an electric field.

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