FERROELECTRICITY AND CRYSTAL-LATTICE DYNAMICS

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INTRODUCTION

THE ideas amassed in recent years about the physical nature of ferroelectricity are the consummation of a rather important stage in the development of the microscopic theory. The latter includes the model theories of Mason and Matthias,[1] Ginzburg,[2] Devonshire,[3] Slater,[4] and other authors.[5-7]

As applied initially to the simplest type of ferroelectric materials having the BaTiO$_3$ structure, the cited phenomenological and model theories have essentially amounted to formulating conditions equivalent to a so-called "polarization catastrophe," which results in an unbounded increase in the static dielectric constant at the phase-transition point. However, these theories have not considered in detail the dynamic processes in crystal structures. This has restricted the possibilities of analyzing and explaining certain experimental data (in particular, the vibrational spectra of ferroelectric crystals) that began to appear in the literature rather frequently as early as the middle fifties.

The fruitful ideas of Anderson,[8] Ginzburg,[2, 9] and Cochran[10, 11] have attained wide recognition in recent years. According to these, a phase transition to the ferroelectric state can be treated from the standpoint of the stability of the crystal structure with respect to certain normal vibrations. Evidently, this approach can be applied only to phase transitions accompanied by a rearrangement of the crystal structure with a change in the elastic bonds in the crystal. It rules out phase transitions of the relaxation type (e.g., of the "order-disorder" type). These ideas have since been developed in a series of other articles,[12-14, 99] and have made it possible not only to reconsider earlier theoretical ideas, but also directly to relate the theory of ferroelectricity to other branches of crystal physics within the framework of the dynamic theory of crystal structures.[15] On the other hand, they have powerfully stimulated the development of goal-directed studies, which have subsequently confirmed the fundamental assumptions of the dynamic theory, at least as applied to ferroelectric materials of the BaTiO$_3$ type.

We must emphasize that all of the most important and characteristic features of the vibrational spectra of ferroelectric crystals and their variations in the phase-transition region are described by the phenomenological theory of ferroelectricity. However, this does not exclude another approach to the problem of ferroelectricity based on concrete analysis of the microscopic interatomic bonds in the crystal, which

determine the nature of the vibrations of the crystalline substructures.

This review is an attempt to present the current progress of the theoretical approach to the problem of ferroelectricity from the standpoint of crystal dynamics, and also to discuss on this level the corresponding experimental data obtained by different methods.

1. THE DYNAMIC APPROACH TO THE PROBLEM OF FERROELECTRICITY

It is not hard to see that, in substances that undergo a phase transition involving a rearrangement of the crystal structure and a change in the elastic bonds between the atoms, the vibrational spectrum must also change substantially as we approach the phase-transition point. This assumption is equally true of a large number of ferroelectric crystals.

Ginzburg[2] stated in 1949 the first theoretical ideas on the features of the vibrational spectra of ferroelectric crystals in the phase-transition region. He established the relation between the dispersion parameters of the oscillator describing the polarization of the ferroelectric substance and the parameters of the phenomenological theory. He derived this relation by comparing the equation of motion of the oscillator in an external field

$$\mu \ddot{P} + v \dot{P} + kP + sP^3 = \frac{E_0}{2} e^{i\omega t} \qquad (1)$$

at $\omega = 0$ with the corresponding condition that the thermodynamic potential

$$\Phi = \Phi_0 + \alpha P^2 + \frac{\beta}{2} P^4 + \ldots \qquad (2)$$

should be a minimum. Consequently, in the terms of the phenomenological theory, the well-known dispersion formula for such a vibration takes on the form

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{A_i}{\omega_i^2 - \omega^2 + i\gamma\omega} = \varepsilon_\infty + \frac{2\pi/\mu}{\frac{\alpha}{\mu} - \omega^2 + i\frac{v}{\mu\omega}}. \qquad (3)$$

Here we must first consider the fact that the resonance frequency ω_i of the oscillator is expressed in terms of the coefficient α of the thermodynamic potential series in the form $\omega_i = \sqrt{\alpha/\mu}$, where $\mu = m/2e_{eff}^2 N$, and m is the reduced mass of the vibration. Thus, the anomalous properties of this vibration are completely determined by the nature of the temperature dependence of the parameter $\alpha = \alpha_\theta' (T - \theta)$, where θ is the phase-transition point, and α_θ' is a constant. In particular, this implies that the frequency of the given vibration must be exceedingly low in the phase-transition region, and that it should approach zero as we approach the phase-transition point according to the law

$$\omega_i = \sqrt{\frac{\alpha_\theta'}{\mu}} (T - \theta)^{1/2} = const \cdot (T - \theta)^{1/2}. \qquad (4)$$

The value of ω_i estimated in these studies for $BaTiO_3$

proved to be $\omega_i \cong 3 \times 10^{11}$ cycles/sec, taking $\alpha \sim 10^{-3}$ and $\mu = 10^{-26}$ (for a model in which Ba vibrates with respect to TiO_3). This corresponds to a wavelength $\lambda_i = 2\pi c/\omega_i \cong 6$ mm. Ginzburg[9] later developed these ideas for the case of first-order phase transitions. Here he showed that when $T > \theta$, the following expression continues to hold:

$$\omega_i = \sqrt{\frac{\alpha_\theta'}{\mu}} (T - T_C)^{1/2} = const (T - T_C)^{1/2}, \qquad (5)$$

with the difference that the Curie temperature (T_C) differs in this case from the phase-transition temperature (θ). Hence, the frequency of the given vibration approaches a finite value of the phase-transition point:

$$\omega_i(\theta) = \sqrt{\frac{\alpha_\theta'}{\mu}} (\theta - T_C)^{1/2}. \qquad (5')$$

In the tetragonal phase, the frequency of the corresponding vibration at $T = \theta$ has the different value:

$$\omega_{zi}(\theta) = 2\sqrt{\frac{\alpha_\theta'}{\mu}} (\theta - T_C)^{1/2}. \qquad (5'')$$

For $BaTiO_3$, which has a first-order phase transition, the precise value of ω_i right at the phase-transition point proved to be of approximately the same order of magnitude, namely, $\omega_i \sim 6 \times 10^{11}$ cycles/sec, and $\lambda_i \sim 3$ mm, while for the tetragonal phase $\omega_{zi} \sim 1.2 \times 10^{12}$ cycles/sec, and $\lambda_{zi} \sim 1.5$ mm.[9]

Thus, in accord with the phenomenological theory, the fundamental features of the vibrational spectra of ferroelectric crystals are the existence of a low-frequency normal vibration closely involved in the ferroelectric properties of the crystal, and a considerable frequency decrease and a change in the other parameters of this vibration as we approach the phase-transition point.

On the other hand, it is evidently desirable to concretize these parameters as applied to individual ferroelectric materials of any given structural type. Such a concretization presupposes the use of crystal-chemical data on the packing and nature of the chemical bonding of the atoms in the crystal structures of the ferroelectric materials. It therefore becomes possible to establish a relation between the features of the vibrational spectra and various semi-empirical crystal-chemical criteria and model theories of ferroelectricity.

In this case, the basis of analyzing the vibrational spectra of the crystal is to solve the system of equations of motion of the atoms of different types in the force field of all the other atoms of the crystal. However, the equations contain a large number of parameters describing the force interaction of the atoms with one another, and many of these cannot be determined experimentally and have to be postulated. Therefore, exact enough calculations can be made at present only on crystals of very simple structures,

perferably with ionic-type bonding. Nevertheless, as Cochran has shown,[10, 11] use of concrete model conceptions of the structure and force interaction of the atoms in crystals permits one to establish physically pictorial relations for the balance of forces determining the dynamic stability of the structures of ionic crystals and their dielectric properties. In view of the pictorial character of the expressions derived by Cochran for diatomic ionic crystals, as well as for ferroelectric crystals of the $BaTiO_3$ type, we shall take up below the content of Cochran's theory without overestimating its significance thereby.

1.1. Lattice Dynamics and Stability of Non-piezoelectric Crystals

Kellermann[24] obtained the first results describing the lattice dynamics of NaCl-type ionic crystals by using a model of rigid non-polarizable ions. As it turned out, the rigid-ion model is a rather poor approximation. Consequently, it has been necessary to take the polarizability of the ions into account to get satisfactory agreement with experiment, even for classical ionic crystals.[12, 13] Evidently, a correct account of the polarizability of the ions is an even more important factor among the "ionic" ferroelectric crystals of the $BaTiO_3$ type, since the polarization of the electron shells of the ions is responsible for more than two-thirds of the spontaneous polarization of these crystals.[4, 49, 62]

A systematic account of the polarizability of the ions has been made in the series of alkali-halide crystals,[12, 13] and also for $SrTiO_3$,[14] based on the so-called shell model proposed by Dick and Overhauser.[101] According to this model, the crystalline substance is considered to consist of atomic cores (nuclei + inner filled electron shells) distributed at the sites of the structure. That is, it consists of ions and outer electron shells. The cores and shell are treated as independent substructures bound together by short-range forces and also by long-range electrostatic forces. This description of the properties of the crystal takes into account the interactions between the different ions, between the ions and the electrons of other ions, and also electron-electron interactions.

Cochran[10, 11] has made a further analysis of the possibilities of the shell model as applied to the problem of ferroelectricity, based on the concept of polarization of ionic crystals, as developed in the papers of Tolpygo and Mashkevich.[16]

a) General vibration equations and the condition of structural stability. Let the equilibrium position of the k-th atom (k = 1, ..., n, where n is the number of atoms in the unit cell) in the l-th unit cell be defined by the vector $r(lk) = r(l) + r(k)$, and the displacements of the ions from their equilibrium positions and those of the electrons with respect to their ions be de-

noted respectively by $u(lk)$ and $w(lk)$. Then, in the harmonic approximation, the increment of the lattice energy involved in these displacements is a quadratic function of the displacements $u(lk)$ and $w(lk)$, and has the following form:

$$
\begin{aligned}
\Phi = -\frac{1}{2} \sum_{lk\alpha} \Big\{ & \sum_{l'k'\beta} [\Phi^R_{\alpha\beta}(lk, l'k')\, u_\alpha(lk)\, u_\beta(l'k') \\
& + Y^{-1}_k \Phi^T_{\alpha\beta}(lk, l'k')\, u_\alpha(lk)\, p_\beta(l'k') \\
& + Y^{-1}_k \Phi^T_{\alpha\beta}(l'k', lk)\, p_\alpha(lk)\, u_\beta(l'k') \\
& + Y^{-1}_{k'},\, Y^{-1}_k \Phi^S_{\alpha\beta}(lk, l'k')\, p_\alpha(lk)\, p_\beta(l'k') \\
& + \alpha^{-1}_k p^2_\alpha(lk) + [p_\alpha(lk) + Z_k u_k(lk)]\, E_k(lk) \Big\},
\end{aligned}
\tag{1.1}
$$

where the subscripts α and β refer to the different components of the vector quantities, and Z_k and Y_k are numbers determining the effective electric charges of the ions and electrons, respectively, of the k-th type, in electronic-charge units. Here the expressions $\Phi^R_{\alpha\beta}$, $\Phi^I_{\alpha\beta}$, and $\Phi^S_{\alpha\beta}$ are the force constants representing the short-range forces between ions, between ions and electrons, and between electrons, respectively. The term $\alpha^{-1}_k p^2_\alpha(lk)$ takes into account the electrostatic interaction of the electrons with their ions, while the coefficient of $E_k(lk)$ in square brackets is the total Coulomb interaction of all the electrons and ions in the crystal. Here α_k is the electronic polarizability of the k-th ion, $p(lk) = Y_k w(lk)$ is the dipole moment produced when the electron is displaced with respect to its core, and $E_k(lk)$ is the effective field acting on the k-th ion.

Let us consider the mass of an electron to be negligibly small, i.e., concede that the electron will move with the field without inertia at the frequencies in question. Then the equations of motion are determined, as usual, from the condition of equilibrium of forces. For the ions and electrons, respectively, this is:

$$
\begin{aligned}
m_k \ddot{u}_\alpha(lk) &= -\frac{\partial \Phi}{\partial u_\alpha(lk)}, \\
0 &= -\frac{\partial \Phi}{\partial p_\alpha(lk)},
\end{aligned}
\tag{1.2}
$$

where m_k is the mass of the k-th ion. Further, we shall assume that the displacements $u(lk)$ of the ions and $w(lk)$ of the electron and the other quantities associated with them can be represented in the form of normal vibrations of the type

$$
u(lk) = U(k) \exp i\,[qr(lk) - \omega t],
\tag{1.3}
$$

where q is the wave vector (q = $2\pi/\lambda$), and λ and ω are the wavelength and frequency of the corresponding normal vibration. If we assume that the force constants are periodic functions of l, and depend on the difference $l - l'$, rather than on their absolute values values (see [15]), then, upon substituting expressions like (1.3) into (1.2), we get the following system of 3n equations:

$$\omega^2 m_k U_\alpha (k) = \sum_{k'\beta} [R_{\alpha\beta} (kk') + Z_k C_{\alpha\beta} (kk') Z_k] U_\beta (k')$$
$$+ \sum_{k'\beta} [T_{\alpha\beta} (kk') + Z_k C_{\alpha\beta} (kk') Y_{k'}] W_\beta (k'),$$
$$0 = \sum_{k'\beta} [T_{\alpha\beta} (kk') + Z_k C_{\alpha\beta} (kk') Y_{k'}] U_\beta (k')$$
$$+ \sum_{k'\beta} [\Phi_{\alpha\beta} (kk') + Y_k C_{\alpha\beta} (kk') Y_{k'}] W_\beta (k').$$

$$(1.4)$$

Here we have introduced symbols for $R_{\alpha\beta}(kk')$, $T_{\alpha\beta}(kk')$, and $S_{\alpha\beta}(kk')$ of the type

$$R_{\alpha\beta} (kk') = -\sum \Phi_{\alpha\beta}^R (lk, \ l'k') \exp iq [r (l'k') - r (lk)], \quad (1.5)$$

whereas

$$\Phi_{\alpha\beta} (kk') = S_{\alpha\beta} (kk') + \delta_{\alpha\beta}\delta_{kk'}\alpha_k^{-1} Y_k^2. \quad (1.6)$$

The quantities $C_{\alpha\beta}(kk')$ are the structure coefficients of the internal field acting in the polarized crystal (see, e.g., [4, 5]). Here the field amplitudes E_α acting on the ion and the electron of the k-th type are

$$E_\alpha (kk') = \sum_{k'\beta} C_{\alpha\beta} (kk') [Z_{k'} U_\beta (k') + Y_k W_\beta (k')]. \quad (1.7)$$

It is useful to note that the set of all possible quantities occurring in (1.4) can be represented in the form of corresponding matrices. Then Eqs. (1.4) can be written in the more convenient matrix form

$$\omega^2 m_d U_c = (R + Z_d C Z_d) U_c + (T + Z_d C Y_d) W_c,$$
$$0 = (\tilde{T} + Y_d C Z_d) U_c + (\Phi + Y_d C Y_d) W_c. \quad (1.8)$$

By eliminating W_C from these equations, we obtain equations for the displacements of the ions alone:

$$\omega^2 m_d U_c = M U_c. \quad (1.9)$$

where the matrix M defines the effective force constants characterizing the interaction of the substructures, and has the form

$$M = R + Z_d C Z_d - (T + Z_d C Y_d) (\Phi + Y_d C Y_d)^{-1} (T + Y_d C Z_d). \quad (1.10)$$

The system of homogeneous equations (1.9) can be solved if its principal determinant $[M - \omega^2 m_d]$ is zero. That is,

$$[M_{\alpha\beta} (kk') - m_k\omega^2\delta_{\alpha\beta}\delta_{kk'}] = 0. \quad (1.11)$$

This so-called secular equation determines in the general case the frequencies of all 3n normal vibrations of the crystal structure for a fixed value of the wave vector q. It also determines the relation $\omega = f(q)$ of the frequency of each normal vibration to q, i.e., the dispersion law describing the 3n branches of the lattice-vibration spectrum.

As is known, all the vibrations can be classified as acoustic or optical. In the former case, the ions of the unit cell move in phase (Fig. 1). That is, individual macroscopic regions of the specimen move as a whole. Naturally, in crystals showing no piezo-effect, such a vibration does not involve the appearance of a time-dependent electric moment. For q = 0, the acoustic vibrations correspond to the trivial solution $\omega = 0$ of the system of equations (1.11). In the latter case, the
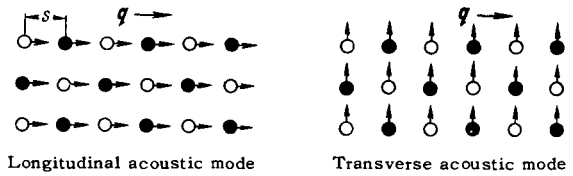

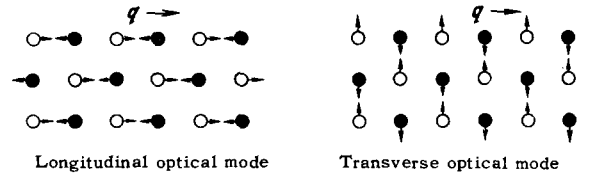FIG. 1. Acoustic vibrations of a one-dimensional chain of ions.

FIG. 2. Optical vibrations of a one-dimensional chain of ions.

vibrations amount to an out-of-phase motion of the oppositely charged ions of the unit cell (Fig. 2). These vibrations in general give rise to an oscillating dipole moment of the unit cell, and form running electromagnetic waves. They are called optical because they can interact with the electromagnetic field of optical radiation. We note that the frequencies of the optical branches do not approach zero as q → 0, and generally remain finite for infinitely long wavelengths.

One can distinguish between longitudinal and transverse vibrations, depending on the direction of the polarization vector of the vibrations with respect to the wave-propagation direction (see (1.3)). In general, there are twice as many transverse as longitudinal vibrations. However, the transverse vibrations can be doubly degenerate in special cases of crystals of high enough symmetry. For illustration, Fig. 3 shows the different vibrational branches of frequencies of NaCl, as calculated in [24].

An important fact that will be of primary importance later on in discussing situations favoring the existence of a ferroelectric transition is the difference between the values of $\omega(q)$ for transverse and longi-
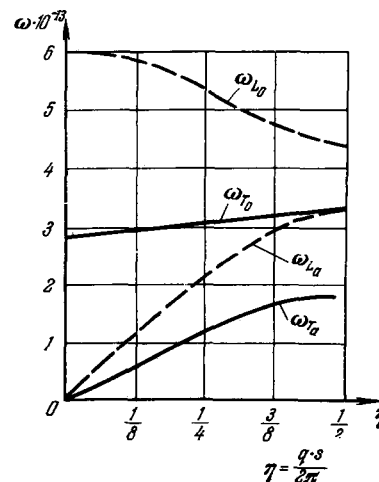

FIG. 3. Calculated acoustic and optical branches of the lattice-vibration spectrum of NaCl according to Kellermann.[42]

tudinal vibrations. This involves the fact that the components of the effective field parallel and perpendicular to the direction of propagation of the vibration differ substantially from one another. We can see this clearly by analyzing the Coulombic terms contained in M. This feature becomes more evident in the more interesting case of long waves in simple crystals of high symmetry. As we know, the field acting on an ion in a polarized crystal structure is equal to the sum of the average macroscopic field E_{macr} and the field E_1 accounting for the action of the dipoles distributed within the so-called Lorentz sphere:

$$E_{eff} = E_{macr} + E_1. \tag{1.12}$$

Leaving aside the problem of the values of the field E_1 (which, for example, is zero for diatomic cubic crystals), according to [15] we have for $q \to 0$:

$$E_{macr} = -\lim_{|q| \to 0} \frac{4\pi}{v} \left(\frac{q}{|q|} \right) \left(\frac{q\mu}{|q|} \right), \tag{1.13}$$

where μ is the dipole moment of the unit cell, and v is its volume. This implies that $E_{macr \perp q} = 0$, whereas $E_{macr \parallel q} \neq 0$. In particular, for diatomic cubic crystals

$$E_{macr \parallel q} = -\frac{4\pi\mu}{v} = -4\pi P, \tag{1.14}$$

where P is the electric moment of the crystal. Thus, the crystal structure is more rigid for longitudinal vibrations, and their frequencies are always higher than those of the corresponding transverse vibrations.

A necessary condition for the stability of a vibrational process occurring in a crystal is that all of its characteristic frequencies should be real, as determined by the determinantal equation (1.11). If the frequencies are not real, two paired complex conjugate roots should exist. One of these leads to an increase in time of the vibrational amplitude in (1.3). This is equivalent to breakdown of the structure or to some change in it that makes the vibrations become stable again. In line with a well-known theorem,[17] the condition that only positive solutions should exist is satisfied when all the principal minors of the determinant composed of the elements of the matrix M are positive. That is,

$$\text{Det}^{3(n-1)} |M| > 0. \tag{1.15}$$

Hence, the vanishing of one of the principal minors of (M) is equivalent to a non-trivial solution $\omega = 0$ of the system (1.11), and indicates that the given crystal structure is unstable.

Condition (1.15) is a general expression determining the stability of a crystal, upon which a theory of the corresponding phase transitions could be based.

Evidently, if we want to obtain the temperature-dependences of the parameters M which are responsible for the breakdown in condition (1.15) at a certain temperature, we must not restrict the treatment to the purely harmonic approximation of the original equations (1.4). We should note that the introduction of anharmonicity into these equations, even if treated as a small perturbation, considerably complicates the whole problem (see, e.g. [19]). This is because the normal character (i.e., the independence) of the vibrational modes proves to be violated, strictly speaking. Cochran's theory avoids this difficulty either by postulating the temperature-dependences of the parameters M, or by introducing them in a non-rigorous way, starting with a comparison with the expressions arising from the phenomenological formulations. This renders the condition of stability less "effective" and limits the possibilities of analyzing the microscopic mechanism responsible for the phase transitions in terms of the dynamic theory. Furthermore, the application of the condition (1.15), even in the harmonic approximation, is per se the only more or less systematic attempt thus far to relate the vibrational spectrum of crystals to features of the phase transitions in cases where this relation can be made.

In determining phase-transition points involving a change in the symmetry of a crystal, it proves useful to find the point at which condition (1.15) breaks down for any particular mode of vibration. In this case, one can simplify the structure and reduce the order of the minors of M. As we shall see below, another advantage of treating the breakdown of the stability of crystals for one particular mode is that one can make a more definite interpretation of the physical mechanism giving rise to it.

Since the vibrations of the acoustic branch generally do not give rise to electric fields in the crystal, it is natural to relate instability of the electrical state of the crystal (a ferroelectric transition) to instability of the system of electric oscillators. That is, condition (1.15) fails for the frequencies of the optical branch of the spectrum. Here the case of greatest interest is when the frequencies of the optical branch become anomalously low as $q \to 0$, i.e., infinitely long waves corresponding to in-phase vibrations of ions of like sign in the crystal, or in other words, vibrations of the substructures as a whole. It is precisely to this type of vibration that we can ascribe an oscillating macroscopic electric moment P. The reason for this is that when λ is comparable with the dimensions of the crystal, mutually compensating regions are formed in it, having oppositely directed dipoles. Hence, $P = 0$. We must note that this statement, which serves as the fundamental tenet in the dynamic approach to the theory of ferroelectricity, is at the same time a "zero-order approximation." As will become clear later on, it holds true only for non-piezoelectric crystals. Furthermore, it is assumed here implicitly that the velocity of propagation of electromagnetic waves is infinite, and that there are no reflections from the crystal boundaries.

b) Dielectric properties of crystals and their re-
lation to the characteristic frequencies. Using the
equations derived above, it is not hard to write an ex-
pression for the dielectric constant $\epsilon(\omega)$ in the pa-
rameters of the dynamic theory for the case $q \to 0$.
This is of especial interest, since the behavior of $\epsilon(\omega)$
in the vicinity of a phase transition is well known for
many ferroelectric crystals. First we shall derive
this expression and then comment on it as applied to
cubic non-piezoelectric crystals. With certain as-
sumptions made, the results of this treatment can be
applied to ferroelectric materials of perovskite-type
structures, in particular, to $BaTiO_3$. As will be shown
below, the difference between "ionic" ferroelectric
crystals like $BaTiO_3$ and simple ionic crystals like
NaCl consists only in a differing quantitative balance
of attractive and repulsive forces. This is of no fun-
damental importance in the qualitative description of
ferroelectricity in terms of lattice dynamics. In es-
sence, the expressions derived here determine the
conditions under which simple ionic crystals could
become ferroelectric.

The behavior of a crystal in an external alternating
field $E = E \exp(-ipt)$ can be described by equations
similar to (1.8):

$$p^2 m_d U_c = (R + Z_d C Z_d) U_c + (T + Z_d C Y_d) W_c - e E_A Z_c,$$
$$0 = (T + Y_d C Z_d) U_c + (\Phi + Y_d C Y_d) W_c - e E_A Y_c. \qquad (1.16)$$

The expression for $\epsilon(p)$ can be derived by using
the well-known formula

$$\epsilon(p) = 1 + 4\pi \frac{P}{E_A}, \qquad (1.17)$$

where

$$P = \frac{e}{v}(Z_r U_c + Y_r W_c). \qquad (1.18)$$

If the field frequency p is so high that the ions
can't follow the variations in the field E_A, then the
ionic displacements $U_c = 0$. Thus, we have the follow-
ing expression for the high-frequency dielectric con-
stant:

$$\varepsilon_\infty = 1 + 4\pi \frac{e^2}{v} Y_r (\Phi + Y_d C Y_d)^{-1} Y_c. \qquad (1.19)$$

Analogous considerations presented in detail in [10]
give an expression for the dielectric constant at an
arbitrary field frequency p. For the static dielectric
constant ($p = 0$), it takes on the form:

$$\varepsilon_0 = \varepsilon_\infty + 4\pi \frac{e^2}{v} [Z_r''] [\text{Det } M]^{-1} [Z_c''], \qquad (1.20)$$

where $[Z_r'']$ and $[Z_c'']$ are numbers characterizing the
effective dynamic charges of the ions with account
taken of overlap of electron shells and interaction of
the corresponding ionic sublattices. They are the ele-
ments of the matrices Z_r and Z_c whose indices cor-
respond, respectively, with those of the columns and

rows deleted in deriving the principal minor of
[Det M].

The fundamental conclusion from the derived ex-
pression (1.20) is that it shows directly that the di-
electric constant approaches infinity when [Det M]
$\to 0$ (as we have noted, this is involved in a phase
transition), while the frequency ω of the correspond-
ing vibration approaches zero. As we showed at the
beginning of this article, this result is implied in
principle by Ginzburg's[2] phenomenological theory,
and has a very simple meaning. We recall that ϵ_0
and ω_i are connected by the simple relation ϵ_0
$= \epsilon_\infty + A_i/\omega_i^2$ in the dispersion formula (2), if we neg-
lect damping. Then the condition $\omega \to 0$ must imply
that ϵ_0 approaches infinity. The well-known Lyddane-
Sachs-Teller[21] formula contains a direct relation
between the dielectric constant and the transverse and
longitudinal vibration frequencies ω_T and ω_L for di-
atomic alkali halide crystals:

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \frac{\omega_L^2}{\omega_T^2}. \qquad (1.21)$$

Cochran[10] has generalized this formula to the case
of cubic crystals having an arbitrary number of sub-
lattices:

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \prod_{j=2}^{n} \frac{(\omega_j)_L^2}{(\omega_j)_T^2}, \qquad (1.22)$$

where the term for j = 1, corresponding to acoustic
vibrations having $\omega_1 = 0$, has been omitted from the
product.

If we assume that ϵ_0 varies with the temperature
according to the Curie-Weiss law, then the latter ex-
pression implies that the temperature-dependence of
ω_T must have the form $\omega_T \sim (T - T_C)^{1/2}$, since ω_L
can vary only over a small range, as has been stated.
This $\omega_T(T)$ relation agrees with the data of Ginzburg's
phenomenological theory (see Eq. (4)).

c) The physical mechanism of the ferroelectric
transition in cubic crystals. The equations discussed
in the last section permit us to formulate in a rather
general form the conditions of stability of lattice vi-
brations and to establish relations connecting the di-
electric constants ϵ_0 and ϵ_∞ with the normal vibration
frequencies. However, we can define the physical
mechanism responsible for the phase transition only
to the extent that we concretize the initial model of
the crystal. Within the framework used in deriving
the fundamental relations of the shell model, the ques-
tion remains unanswered why condition (1.15) breaks
down at a particular temperature, i.e., why there is a
phase transition. In this regard, it is useful to apply
the theory developed in the last section to two crystals
of cubic symmetry: a non-ferroelectric one, i.e., any
of the alkali-halide crystals (e.g., NaCl), and the typi-
cal ferroelectric substance $BaTiO_3$.

As applied to an NaCl-type crystal, the equations
(1.4) can be written in the form

$$m_1\omega_T^2 U_1 = R_0(W_2 - U_1) + \frac{4\pi}{3}PZe,$$
$$m_2\omega_T^2 U_2 = R(W_2 - U_2) + \frac{4\pi}{3}PXe, \qquad (1.23)$$
$$0 = R(U_2 - W_2) + R_0(U_1 - W_2) + \frac{4\pi}{3}PYe,$$

Here we assume that only the negative ions are polarizable, and denote the displacements by U_1, U_2, and W_2, and the effective charges of the positive ions, the cores, and outer shells of the negative ions, respectively, by Ze, Xe, and Ye. Here R and R_0 are the short-range force constants, and the last term on the right-hand side of the equations describes the electrostatic force. In the transverse-wave case under consideration, the effective field is equal to the Lorentz field $(4\pi/3)P$. We assume here, again for simplicity, that the wave vector $q \approx 0$ and lies along the crystallographic direction [100], while the sublattices are displaced in the transverse direction [001], so that $q \cdot r = 0$ in (1.3).

If we eliminate from (1.23) the displacements W_2 of the electron shells, taking into account the fact that the polarization $P = (e/v)(ZeU_1 + XeU_2 + YeW_2)$, we get an equation resembling (1.9) for the relative displacements of the ions:

$$\omega_T^2\mu(U_1 - U_2) = \left[R_0' - \frac{4\pi}{9v}(Z'e)^2(\varepsilon_\infty + 2)\right](U_1 - U_2), \quad (1.24)$$

where $\mu = m_1 m_2/(m_1 + m_2)$, $R_0' = RR_0/(R + R_0)$, and $Z' = Z + YR_0/(R + R_0)$. In deriving this equation, we have used the condition of electroneutrality of the crystal and the fact that we can express certain constants in terms of the polarizability $e/v \cdot (Ye)^2/(R + R_0) = \alpha$, using equations of motion like (1.23) in an external high-frequency field for which $U_1 = U_2 = 0$. Then we replace them by the simpler quantity ε_∞, since according to the Clausius-Mosotti formula
$\alpha = (v/4\pi)(\varepsilon_\infty - 1)/(\varepsilon_\infty + 2)$.

The analogous equation for longitudinal waves is derived in the same way, except that, as was shown earlier (see (1.14)), the effective field here is $(4\pi/3)P - 4\pi P = -(8\pi/3)P$:

$$\omega_L^2\mu(U_1 - U_2) = \left[R_0' + \frac{8\pi}{9v\varepsilon_\infty}(Z'e)(\varepsilon_\infty + 2)\right](U_1 - U_2). \quad (1.25)$$

Thus, the condition (1.15) that one of the principal minors of M should vanish in the phase-transition region, which is equivalent to the vanishing of the frequency of a certain transverse vibration, takes on the concrete form

$$R_0' - \frac{4\pi}{9v}(Z'e)^2(\varepsilon_\infty + 2) = 0. \qquad (1.26)$$

As we see from (1.25), for longitudinal vibrations the right-hand side of the equation consists of two terms of the same sign, and cannot in principle vanish. The physical meaning of the condition (1.26) is evident, and corresponds to the results of the Ginzburg-Devonshire-Slater theory. According to the latter, the cri-

terion of a phase transition is that the short-range forces acting to restore a displaced ion to its original position should equal the long-range electrostatic forces acting to displace it. This relation is sometimes called the criterion of ferroelectric activity.[22, 23]

In order that ω_T^2 should vanish, and should vary with the temperature according to the Curie-Weiss law in accord with Eqs. (4) and (1.22), it suffices to assume that in the phase-transition region

$$1 - \frac{1}{R_0'}\frac{4\pi}{9v}(Z'e)^2(\varepsilon_\infty + 2) \sim (T - T_c), \qquad (1.27)$$

where T_C is the Curie temperature. This relation can be derived in various ways. We can assume that any of the quantities occurring in the second term of (1.26) varies as $1 + \kappa T$, where κT is small in comparison with unity. However, Slater[4] has shown that the temperature coefficients for ε_∞ and for volume expansion are too small, and that the only reasonable explanation of the relation (1.27) can be obtained if we assume that R_0' depends on the amplitude of displacement of the ion. Here the anharmonicity of the vibrations, or at least of some of them, of the ions of the ferroelectric material is reflected by a formula of the type:

$$R_0' = B_0 + B_1 U^2 + B_2 U^4. \qquad (1.28)$$

From this standpoint, the model used in the dynamic theory hardly differs from the anharmonic-oscillatory model used in [4]. However, the difficulty consists in the fact that introduction of anharmonicity directly into the workings of the dynamic theory, i.e., into (1.4), considerably complicates the problem, even if we consider the non-linear terms of (1.1) to be a small perturbation (see also [18, 19, 120]).

Calculation of the constants occurring in Eq. (1.26) using the atomic parameters of NaCl- and CsCl-type crystal structures[12, 24] shows that for alkali-halide crystals both terms are of the same order of magnitude, but R_0' is about twice as large as the second term. Thus, for example, according to [12] for NaI, the effective charge coefficient of the ions $Z' = 0.69$; $R_0' = 2.89 \times 10^4$ dynes/cm, and $(4\pi/9v)(Z'e)^2(\varepsilon_\infty + 2) = 1.1 \times 10^4$ dynes/cm. In other words, the structure of the discussed alkali-halide crystals proves to be too rigid, the vibrations of the ions are not anharmonic enough, while the polarizabilities are not high enough for mutual compensation of the electric and restoring forces to set in, as we discussed above.

This situation is substantially changed in $BaTiO_3$ and other ferroelectric crystals. Unfortunately, for $BaTiO_3$ we cannot completely concretize all the quantities occurring in (1.11) for lack of the necessary experimental and theoretical data. However, if we make some simplifying assumptions, in particular, that all the oxygen atoms are equivalent, and use numerical values of the structure coefficients C and of the con-

stants R_0', Z, B_1 and B_2 in (1.28), following Slater, we can nevertheless obtain qualitatively the fundamental relations $\epsilon(T)$, $P^2(T)$, and others characterizing the ferroelectric materials. Here it turns out that the long-range and short-range forces compensate one another considerably more fully in $BaTiO_3$ than in the alkali-halide crystals. Consequently, the frequency of the corresponding transverse vibration becomes anomalously low in the phase-transition region.

As was shown at the beginning of this section, an estimate of ω_i at the phase-transition point according to Eq. (5) gives $\omega_i = 6 \times 10^{11}$ cycles/sec. If we assume that the frequencies of the other normal frequencies depend weakly on the temperature, Eq. (1.22) also gives a low value of ω_i. Given a typical variation of $\epsilon_0(T)$ from room temperature to the phase-transition point, ω_i must decrease by a factor of $(\epsilon_0(\theta)/\epsilon_0(T))^{1/2} \sim 50$. That is, while the frequency of this vibration at room temperature $\sim 10^{13}$ cycles/sec, in the phase-transition region it must drop to $\sim 2 \times 10^{11}$ cycles/sec.

In connection with what we have said, we should note that it would be useful to examine a more extensive set of NaCl-type diatomic crystals with the aim of finding a more complete compensation of forces, and related thereto, an anomalous temperature-dependence of a transverse optical vibration frequency responsible for a ferroelectric transition. In a study of the series of semiconductor crystals PbS, PbTe, GeTe, and SnTe,[102, 121] they found an anomalous variation of a transverse optical vibration frequency with decreasing temperature in SnTe. This fact indicates that such attempts are not pointless.

The problem of how well the conclusions of the theory described above agree with the experimental data is discussed in Sec. 5.

d) The influence of electronic effects. In spite of the general similarity of the concepts of the static and dynamic theories, the shell model is a substantial improvement over the atomic model of a ferroelectric substance. Its advantage consists in enhancing and taking better account of the role of the electrons in the phase-transition mechanism. In the theories of [1, 3, 4], the electronic polarizability was a sort of "mirror" magnifying the polarization due to the displacements of the ions. In this case, the effect of the electronic polarization on the potential function describing the motion of the ions is taken into account only to the extent that the electronic polarization enters into the expression for the long-range forces.

In the shell model, furthermore, the motion of the electrons (although showing no inertia) directly determines the short-range field. One of the features of the shell model is that it takes into account the polarization of the ions due to the vibrations. The question arises of how well the numerical estimates of the phenomenological parameters based on the shell model agree with the experimental data. In this regard, several shell models have been analyzed in [13, 14] for the

cubic crystals NaI and KBr, and the dielectric constant, elastic constants, the heat capacity, and dispersion curves were calculated. The parameters of the models were determined from the condition of minimum deviation of the calculated macroscopic quantities from their experimental values. They proposed a set of refinements to the ionic model of the alkali-halide crystals described in Sec. 1.2a: a) they took into account not only the short-range forces between nearest neighbors, but also those with the layer of next-nearest neighboring ions (model II); b) they varied the effective charges of the ions (model III); c) they introduced the polarizabilities not only of the negative, but also of the positive ions, including also the "mechanical" polarizabilities due to the asymmetric action of the short-range forces exerted by the vibrating ions (models IV, V, and VI). Each of the models contains its predecessor and supplements it. As we should expect, the later models give the best agreement with experiment. The values of the charges of the ions estimated in [14] for the best model for $SrTiO_3$ ($Z_{Sr} = 0.83$; $Z_{Ti} = 4.91$; $Z_0 = -1.91$) showed that the bonds in $SrTiO_3$ are to a considerable extent ionic rather than covalent.

Dvorak and Janovec[32] have estimated the effect of the electrons on the dynamic stability of $BaTiO_3$ by directly calculating the vibration frequencies of the different atoms. They showed that introduction of the electronic polarizability of the ions into the calculation leads to a decrease in the vibration frequency with respect to that for rigid non-polarizable ions.

Some attempts undertaken in 1964 at a more systematic and rigorous account of the effect of the electrons, based on analyzing the electronic band structure of perovskite-type crystals, are worthy of serious attention. Silverman[18] has recently reviewed the results of such an analysis, and hence we shall limit ourselves here to listing briefly the qualitative conclusions. The analysis of the electronic structure was based on the hypothesis that, in the harmonic approximation, the energy of the crystal is represented as the sum of the energy of the ionic structure, the energy of the valence electrons in the field of the undistorted structure, and finally, a contribution caused by the dependence of the energy of the electrons on the displacements of the atoms and having a direct relation to the lattice dynamics.

According to the data of [109], in an ideal perovskite-type structure the nearest levels to the filled 2p levels of the O^{-2} ions are the free 3d levels for Ti^{3+} ions. Here the size of the energy gap between the 2p levels of oxygen and the various levels of the other ions depends greatly on the value of the ionic charge on oxygen. The observed value of the $2p$ $(O^{2-}) - 3d(Ti^{3+})$ gap is about 3 eV for $SrTiO_3$ and $BaTiO_3$ (this corresponds to 85% ionic character of bonding in $SrTiO_3$[109]). Considering that this is considerably less than the energy difference between other combina-

tions of levels (about 10–15 eV), we can restrict consideration to the interaction between only the stated p and d levels.

In view of the symmetry of the wave functions of these states, each valence p level can interact only with d levels in the conduction band, and vice versa. The energy of the valence p levels is lowered thereby, while the energy of the d levels is increased.

The vibrations of the ions in the paraelectric phase displace them from their equilibrium positions, and thus lead to overlap of the valence wave functions of oxygen with the 3d orbitals of titanium. This is equivalent to the appearance of a covalent interaction, and it adiabatically adjusts itself to the lattice vibrations. Consequently, the electronic ground state of the crystal is described by a system of interacting p and d levels of titanium and oxygen. Here the density of the electron cloud localized on oxygen is attracted toward the titanium. The appearance of static displacements of the ions in the phase transition makes a further constant contribution to the interaction of the p and d levels. Hence, it should enhance the covalent character of the bonds, in accord with Megaw's conclusion.[110]

Analysis shows that the overall change in the energy of the electrons due to the lattice vibrations is negative, in spite of the possibility that the energy of certain d levels may be raised. As applied to the low-frequency vibrations of the $BaTiO_3$ structure discussed here, this negative contribution to the energy of interaction of the atoms, depending on its size, implies a decrease in the vibration frequencies or even a loss of stability of the structure with respect to these vibrations.

Thus, the treatment of the stability of a perovskite-type crystal structure based on a sort of Jahn-Teller effect leads to the same qualitative conclusions that Cochran obtained by basing himself more on a model. Thus, the former approach is no less promising.

1.2. Application of the Theory to Crystals Having Piezoelectric Properties.

An attempt was made in [11] to apply the concepts of the dynamic theory of [10] to ferroelectric substances having more complex symmetry than cubic, and showing a piezoeffect in the paramagnetic region. One of the important features of this case is that one has to consider vibrations of wave number $q \neq 0$. This involves the interaction of waves belonging to the acou acoustic and optical branches of the spectra, as is typical of piezoelectric materials. We should also assign to this category ($q \neq 0$) crystals in which an antiferroelectric configuration sets in at a certain temperature. Thus, the problem is that of trying to treat dielectric, elastic, and piezoelectric anomalies from a unified standpoint, i.e., in terms of stability of the crystal structure.

The theory of the electrostatic properties of crys-

tals has been developed by Born and Kun Huang[15] on the basis of a rigid-ion model. Their theory has been subsequently refined by Cowley,[33] who included in the treatment effects involving electronic polarization. However, taking the electronic polarizability of the ions into account mainly affects the results of quantitative estimates, and does not affect the conclusions on the properties of the crystals being discussed.

In this case the system of equations of motion analogous to (1.9) has the form

$$\omega^2 \mathbf{m}_d \mathbf{U}_c = \mathbf{M} \mathbf{U}_c - \mathbf{Z}_d \mathbf{E}_c, \qquad (1.29)$$

where $\mathbf{E}_c$ is a column matrix whose elements represent the amplitude of the depolarizing macroscopic field (which is $4\pi \mathbf{P}$ for longitudinal waves in a diatomic crystal). In this case we must write the matrix $\mathbf{M}$ as a series expansion in $\mathbf{q}$:

$$M = M^{(0)} + \sum_\gamma M_\gamma^{(1)} q_\gamma + \frac{1}{2} \sum_{\gamma\alpha} M_{\gamma\alpha}^{(2)} q_\gamma q_\alpha + \dots, \qquad (1.30)$$

taking the interaction of the different vibrations into account. Here α, β, and γ are the subscripts denoting the longitudinal and transverse vibrations.

Juast as for the alkali-halide crystals, we can arrive at conditions under which a ferroelectric transition will be observed by a proper choice of the constants characterizing the interaction of the lattice elements and the coefficients of the anharmonic terms. The new feature here, as compared with the results of Sec. 1.1, is that we have to take into account the piezoeffect in the paraelectric phase, i.e., the interaction between the optical and acoustic modes of vibrations. In particular, this can have the result that the crystal can become unstable with respect to a transverse acoustic mode with decreasing temperature, even before it becomes unstable with respect to a transverse optical mode.

In principle, by suitable choice of the crystal constants one can also devise a transition in which crystals (in particular, of the ZnS type) will show antiferroelectric properties.[11,34] For this to happen, we must assume that a transverse optical mode becomes unstable when $q = (0, \pi/2)$. (This corresponds to motion toward one another of ions of the same type situated one lattice repeat apart.) This type of transition can be realized whenever the temperature T_A at which it should be observed proves to be considerably higher than T_C.

The ideas presented here on the mechanism of a ferroelectric transition based on ion displacements can naturally be applied to such well-known ferroelectric materials showing a piezo-effect in the paraelectric phase as Rochelle salt and KH_2PO_4. However, an order-disorder phase transition is apparently more probable for these hydrogen-bonded crystals.[100,104] As we have stated, the ideas presented above are inapplicable to the latter type of transition. Nevertheless, experimental attempts to study these substances from the

described standpoints are undoubtedly of interest. (That is, one might study the changes in the vibrational spectra of these crystals in the vicinity of a phase transition.) Hence, we shall discuss them briefly below below.

2. THE ROLE OF ANHARMONIC EFFECTS AND FLUCTUATIONS AND THEIR MANIFESTATION IN RAMAN SPECTRA

One can explain the temperature variations observed in ferroelectric materials only by taking anharmonic effects into account. As has been noted, it is very hard to solve Eq. (1.2) with account taken of terms of Φ containing powers higher than u^2, even if for no other reason than that normality (i.e., independence) of the different modes of vibration is lost thereby. If we consider that the non-linear terms in (1.1) are small in comparison with the linear components of the vibrations, it naturally becomes possible to use perturbation theory. The assumption that the anharmonic fraction of the energy is small is correct enough in this case (at least, if we exclude the phase-transition point itself). This is implied by the fact that it takes a relatively slight variation of the quantity $R_0'(T)$ in Eq. (1.26) to get the necessary variation of $\epsilon_0(T)$ (as was shown in [4] and then in [10]). Thus, this problem can be solved by thermodynamic perturbation theory combined with using the solutions of the differential equations of the ionic vibrations (i.e., the normal coordinates). The problem of taking anharmonicity into account in terms of the lattice-vibration equations and the perturbation theory was first treated by Born[15] and then by a number of authors.[19, 21] As applied to the problem of ferroelectricity, this method was first used by Anderson.[8]

The essence of the method consists in the following: the state of the crystal is determined by the potential energy, which is expressed in terms of the wave amplitudes u_i^α (transverse and longitudinal) belonging to both branches of the spectrum, i.e., in terms of the entire set of solutions of equations of the type of (1.4) in the harmonic approximation. Here the Hamiltonian H is represented as the sum of two terms: $H = H_0 + H_1$. Here

$$H_0 = \sum_q [S^a(q) U^a_{-q} U^a_q + S^0(q) U_{-q}^0 U_q^0] \qquad (2.1)$$

is the unperturbed portion of the Hamiltonian, composed of the normal amplitudes U_q, which are the solutions of (1.4).

$$H_1 = \frac{1}{N^{1/2}} \sum_{qq'} \lambda^{\alpha\beta\gamma}(q) U_q^\alpha U_{q'}^\beta U_{q-q'}^\gamma + \frac{1}{N} \sum_{qq'q''} \lambda^{\alpha\beta\gamma\delta} U_q^\alpha U_{q+q'}^\beta U_{q+q'}^\gamma U_{q'}^\delta \qquad (2.2)$$

is the anharmonic portion of the Hamiltonian. The summations in Eqs. (2.1) and (2.2) are performed over all the transverse and longitudinal modes belonging to both branches of the spectrum. In the first summation, U_q^0 and U_q^a are the amplitudes, and $S^0(q)$ and $S^a(q)$

are the elastic moduli of the optical and acoustic vibrations, respectively.

Further, we define the free energy as a power series in H_1:

$$A = -kT \ln \int_\tau \exp\left(-\frac{H_0+H_1}{kT}\right) d\tau = A_0 + H_1 + \frac{1}{2kT}[H_1^2 - (H_1)^2].$$

$$(2.3)$$

Here, A_0 is the free energy in the absence of perturbations, the first-order term in H_1 is the quasiharmonic mean of the perturbation of H_0, and the second-order term is the energy fluctuation. We must emphasize that the assumption that the anharmonic fraction of the energy is small, with subsequent expansion of the free energy in a series in the perturbation H_1, is also used in the model theories of Devonshire and Slater[3, 4] and other papers based on the so-called anharmonic-oscillator model. The essential point here is that the Hamiltonian H is expressed in terms of the normal coordinates. This permits one to determine the temperature-dependence of the frequencies of the characteristic vibrations of the structure. Effects due to the electronic polarizability of the ions are not taken into account explicitly in [8]. Construction of the Hamiltonian with account taken of electronic displacements involves no difficulties in principle, and furthermore, makes no qualitative changes in the conclusions that Anderson has drawn. If we apply the minimum-free-energy condition (2.3) in the presence of an electric field, we can determine the value of the dielectric constant $\epsilon_0 = 1 + (4\pi e^2/v^2 S_{eff}^0)$. Here S_{eff}^0 is the effective value (i.e., it takes into account the Coulombic forces) of the optical elastic modulus associated with the vibrational mode $q = 0$. Figure 4 shows the variation of S_{eff} as a function of the wave vector q calculated in [8]. We can easily see that when $q = 0$ in the region $T = \theta$, S_{eff} approaches zero, and hence, $\omega_0 T$ does so also. Correspondingly, at this temperature, $\epsilon_0 \to \infty$.

Thus, it turns out that the physical mechanism responsible for the appearance of ferroelectricity in barium titanate that Anderson used, and the one described above (see Sec. 1.1) lead to the same results.

One of the very important conclusions drawn in [8] on the basis of the estimate (2.2) is that the fluctuations exert a relatively small influence on the nature of the vibrations and the temperature-dependences of the
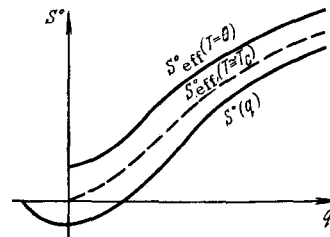

FIG. 4. Theoretical relation of the effective elastic modulus S_{eff} to the wave number q.[8]

macroscopic parameters (ϵ, P, etc.), even in the immediate vicinity of the transition point. However, a variation in the fluctuations near the phase-transition point can lead to very interesting effects involving light scattering.

Ginzburg and Levanyuk[9, 28, 29] have treated in detail the problem of the role of fluctuations in the phase-transition region. For example, the fluctuations in the polarization of the crystal are defined in this case for the point $\mathbf{r}$ as $\Delta P(\mathbf{r}) = P(\mathbf{r}) - P_0$, where P_0 is the polarization for the ordered homogeneous system. The cited studies showed that the fluctuations in P must increase sharply near phase-transition point. This could considerably increase the integral intensity of scattered light in the phase-transition region. Since the fluctuations in $BaTiO_3$ are determined by the displacement of the crystalline substructures, or in other words, by the vibrations, they concluded that this effect should be manifested primarily in the form of Raman scattering. Thus, as the temperature ap - proaches the phase-transition point, besides observing a decrease in the frequency of the ferroelectric vibration and a shift of the corresponding Raman line toward that of the exciting light, we should also observe an appreciable increase in its intensity.

However, we note that it is apparently not always easy to observe this effect. The problem is that the stated vibration is characterized by much damping due to anharmonicity. Hence the Raman-scattering pattern is considerably complicated. According to [28, 29], the spectral distribution of the Raman scattering intensity is described by the formula

$$\mathcal{J}(\omega) = \frac{\left(\frac{v\omega_i^2}{\pi}\right) I}{(\omega_i^2 - \omega^2)^2 + v_i^2\omega^2}, \quad (2.4)$$

where $\omega = \omega_{\text{scattered}} - \omega_{\text{incident}}$, and $I = \int_{-\infty}^{\infty} \mathcal{J}(\omega)$ $\times d\omega$ is the integral intensity of the scattered light. Thus we see that when $v_i > \omega_i$, the Stokes and anti-Stokes components of the Raman scattering merge together, and it becomes impossible to observe them (Fig. 5).

In connection with the problem of the role of the anharmonic terms and fluctuations, we can correlate the data presented above with the equations determining the stability of ferroelectric materials in the terms of the model theories of Mason and Matthias, Devonshire, and Slater.[1, 3, 4] Without taking this point up in detail, we shall only note that the condition for loss of stability of the crystal in the statistical theories is also equivalent to the condition (1.15).[31]

3. TYPES OF NORMAL VIBRATIONS OF PEROVSKITE-TYPE CRYSTAL STRUCTURES

In particular, experimental study of the problems of dynamic stability of ferroelectric crystals permits one directly to test the conclusions of the microscopic theory discussed above. It consists primarily in study-
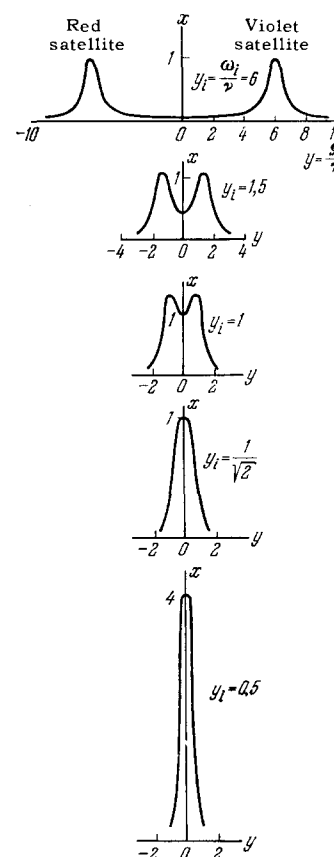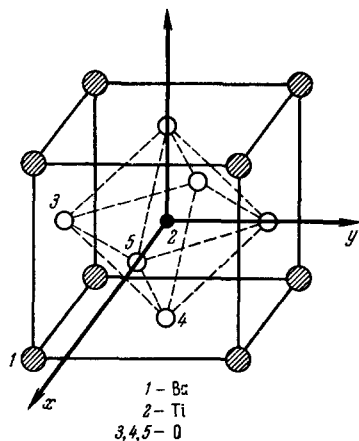

FIG. 5. Variation of the form of the Raman spectrum as a function of the relation between the damping constant and the resonance frequency of the vibration.

ing the features of the vibrational spectra of ferroelectric crystals. Hence, before we proceed to describe the studies along this line, we should use symmetry theory to analyze the form of the vibrational spectra of these crystals, i.e., to determine the number and symmetry type of the expected normal vibrations of their crystal structures.

In line with the general trend of this article, we shall go into more detail in discussing the form of the normal vibrations of crystals having perovskite-type structures. Figure 6 shows the perovskite-type crystal structure. As we know, crystals having this structure can occur in three states, namely, cubic, tetragonal, and orthorhombic. In particular, the $BaTiO_3$ crystal passes through all of these three phases with varying temperature. Last[35] made the first attempt to analyze the vibrational spectrum of this type of crystals. However, this approach was very approximate, and subsequently led to a great variety in interpretations of the experimental results.[36-40] A more correct treatment of the problem of the vibrations of perovskite-type structures was carried out in [32, 41-44], based on the systematic application of group theory. We shall rely hereinafter on the data of these studies.

According to the dynamic theory of crystal structures (see Sec. 1.1), the total number of normal vibra-

FIG. 6. Unit cell of the BaTiO₃ crystal.

tions for BaTiO₃-type crystals should be $3n = 15$. If we exclude the acoustic vibrations, the 12 optical normal vibrations remain.

We shall have to take the symmetry of the crystal into account henceforth in determining the symmetry types and degree of degeneracy of these vibrations. We can do this by using the method proposed by Bhagavantam,[45] which is based on applying group theory to crystals for the case of long waves. A perovskite-type crystal structure in the cubic, tetragonal, and orthorhombic states belongs respectively to the space groups O_h^1–Pm3m, C_{4v}^1–P4mm, or C_{2v}^1–Pmm2.[100, 104] If we take separate account of the translation op-

erations, it is described by the set of symmetry operations appropriate to the groups O_h, C_{4v}, and C_{2v}, respectively. Upon determining the characters of the reducible representations appropriate to these groups for all the symmetry operations by Bhagavantam's method,[45] we can easily calculate by the well-known formula[45] the number of normal vibrations of each symmetry type possible for the given group. Table I gives the results of such a calculation.

We note that, in accordance with the selection rules, vibrations of symmetry types F_{2u} and B_1 (C_{4v}) are forbidden in infrared spectra, while those of symmetry types F_{1u} and F_{2u} are forbidden in Raman spectra.

In order to understand how these vibrations transform as the crystal goes from the cubic to the tetragonal and then to the orthorhombic state (e.g., as one observes in BaTiO₃ with varying temperature), we must construct the corresponding symmetry coordinates. Since a normal coordinate is made up only of symmetry coordinates of the same symmetry type, one can show[42-44] by correlating the symmetry coordinates corresponding to the analyzed types of normal vibrations that the normal vibrations transform as follows upon transition from the cubic to the tetragonal state:

$$F_{1u}(xyz) \rightarrow 1A_1(z) + 1E(xy) \text{ and } F_{2u}(xyz) \rightarrow 1B_1(z) + 1E(xy),$$

where z is the unique fourfold axis. Proceeding to the case of the orthorhombic phase of the perovskite-type crystal structure, we can easily show that the $E(xy)$

Table I. Characters of the reducible representations calculated for all the symmetry operations of cubic, tetragonal, and orthorhombic perovskite crystals, and the number of normal vibrations belonging to the possible symmetry types.

Symmetry groups		O_h										C_{4v}					C_{2v}			
Symmetry operations		E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	E	$C_2(z)$	$\sigma(xz)$	$\sigma(yz)$
Characters of reducible representations	for optical vibrations	12	0	−2	2	−4	−12	−2	0	4	2	12	2	−4	4	2	12	−4	4	4
	for acoustic vibrations	3	0	−1	1	−1	−3	−1	0	1	1	3	1	−1	1	1	3	−1	1	1
Symmetry types of vibrations.*		A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_g	E_u	F_{1g}	F_{1u}	F_{2g}	F_{2u}	A_1	A_2	B_1	B_2	E	A_1	A_2	B_1	B_2
Number of normal vibrations of the given symmetry types	optical	0	0	0	0	0	0	0	3	0	1	3	0	1	0	4	4	0	4	4
	acoustic	0	0	0	0	0	0	0	1	0	0	1	0	0	0	1	1	0	1	1

*F_{1u} and F_{2u} vibrations are triply degenerate, E vibrations doubly degenerate.

vibration degenerate in x and y must split into two different vibrations.

Thus, the infrared absorption spectrum of perovskite-type crystals in the cubic state must consist of three absorption bands corresponding to the vibrations ω_1, ω_2, and ω_3 of the type $F_{1u}(xyz)$. The vibration ω_4 of the type $F_{2u}(xyz)$ is forbidden in the infrared spectra. After the crystal has transformed to the tetragonal state (when measured in unpolarized light), the three above-cited absorption bands should split into doublets of the type ω_i' and ω_i'' (i = 1, 2, 3), and a new band should appear, corresponding to one of the splitting components of the ω_4-type vibration. One of the components of the ω'-type doublets is polarized in the z direction, while the other, ω'', is polarized in the plane perpendicular to this axis. We should expect a further doublet splitting of the E-type vibrations in the infrared absorption spectrum of crystals in the orthorhombic phase, and as a whole, the spectrum should consist of 12 absorption bands.

The Raman spectrum of perovskite-type crystals in the cubic state should show no first-order lines. They are all forbidden by the selection rules. However, after transition of the crystal to the tetragonal phase, the Raman spectrum should manifest all eight vibrations of the types $3A_1(z) + 1B_1(z) + 4E(xy)$. These should apparently have the form of four bands split into doublets, and should depend on the polarization of the light. The Raman spectrum of these crystals in the orthorhombic phase should show all twelve non-degenerate normal vibrations.

The treatment given above has been carried out for q = 0. That is, we neglected the polarization and the direction of propagation of the vibrational waves in the crystal. As has been stated, in certain cases the latter can be classified as transverse (E ⊥ q) and longitudinal (E ∥ q) waves. In other words, we have determined essentially the symmetry types of the normal displacements of the atomic substructures in the crystal. If we take into account the direction of q (even when $|q| \approx 0$), the cited types of vibrations are divided into transverse (2n) and longitudinal (n) types, depending on the chosen direction of q. This does not alter the classification derived above of the normal vibrations of perovskite-type crystals. However, since the frequencies of the longitudinal and transverse vibrations differ considerably, we can expect the appearance of the corresponding lines, e.g., in the Raman spectra.

A very important point in analyzing the phenomenon of ferroelectricity from the standpoint of crystal-lattice dynamics is the problem of the form of the normal vibrations. From the analysis that we have carried out, we can state quite definitely only the form of the normal vibrations of the types F_{2u} and B_1 (in the tetragonal phase). These vibrations involve the relative displacement of only the two crystalline sublattices of the atoms O(3) and O(5) (Fig. 7).
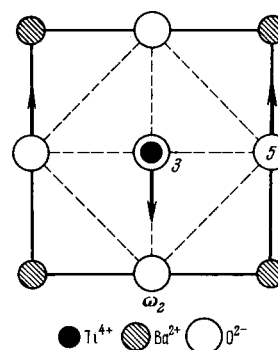
In order to determine approximately the form of

FIG. 7. Form of the normal vibrations of types F_{2u} and B_1 for the perovskite-type crystal structure.

the other vibrations, some authors have introduced certain assumptions corresponding in some degree to reality. Thus, Last[35] started with the differences between the atomic weights and distances between the atoms in the structure, and divided all the atoms of the unit cell into two groups: the cation (e.g., Ba), and the TiO_3 group. As a result, he ascribed the two short-wavelength F_{1u}-type vibrations to internal vibrations of the TiO_6 octahedron, and the longest-wavelength F_{1u}-type vibration to motion of the cation with respect to the TiO_3 group. Other investigators[36, 37, 39] have adopted the same viewpoint. This hypothesis is also favored by the similarity of the observed absorption spectra in the near infrared, as contrasted with their sharp differences in the far infrared, among crystals of perovskite-type structures ($SrTiO_3$, $PbTiO_3$, $BaTiO_3$, etc.), and among crystals of differing structures, but containing TiO_6 octahedra (ilmenite and spinel structures).[35, 44, 47, 48] Hence, the longest-wavelength vibration depends essentially on the mutual displacements of the cations of the Ba and Ti types. Some estimates made by studying the absorption spectra of $BaTiO_3$ in the far infrared also show that a certain relative displacement of the atoms Ti and O(4) must occur in this vibration.[49] These are the ideas on the fundamental features of the low-frequency vibration. As we shall see below, it is more closely related than the other vibrations to the ferroelectric state of $BaTiO_3$-type crystals. We should add in connection with the data from X-ray analysis that the oxygen octahedron is apparently slightly deformed in this vibration.[10]

We have paid major attention in our review to crystals having a perovskite-type structure. However, we shall also have to treat crystals of other structures, e.g., Rochelle salt, KH_2PO_4, $NH_4H_2PO_4$, $NaNO_2$. In particular, we shall encounter these crystals in the section concerned with studying Raman spectra. Here we shall not consider the symmetry of the normal vibrations of these crystals. It is determined by precisely the same methods as were described above, and we shall simply refer the reader respectively to the papers in which these calculations were performed (see, e.g., [50, 51]).

4. FEATURES OF THE EXPERIMENTAL STUDY OF THE DYNAMICS OF FERROELECTRIC CRYSTALS

The first experimental results on the dynamics of $BaTiO_3$ and a number of related compounds were obtained by infrared (IR) spectroscopy and Raman scattering (RS) of light[35, 36, 52] in the late Fifties, i.e., when the features presented above of the vibrational spectra of these compounds were not yet known. These results were incomplete, and the main point was that they proved to be disillusioning in the sense that the studied spectral region showed practically no changes in the vibrational spectra that might be expected intuitively in the vicinity of the phase transition from the paraelectric to the ferroelectric state. The theoretical studies that have appeared in recent years have made possible a fresh approach to explaining the previously-obtained experimental data, and have stimulated a considerable development of spectroscopic studies of ferroelectric substances, but now exactly aimed at their goals. These studies have also predetermined some features of principle in studies of the vibrational spectra of ferroelectric crystals that should be considered in performing experiments.

First of all, the essential distinguishing feature of ferroelectric crystals is that their vibrational spectra should contain a normal vibration closely related to the ferroelectric properties of the crystal (we shall call it the "ferroelectric" vibration), and characterized by a very low frequency. As has been shown, the frequency can attain a value of $\sim 10^{11}$ Hz in the phase-transition region. That is, it lies in the far infrared. Experiments performed in recent years have confirmed this estimate.

Another peculiarity of ferroelectric crystals is the fact that a region of extreme dispersion of the dielectric constant must occur near the frequency of this vibration. For example, the dielectric constant should vary by almost two orders of magnitude for $BaTiO_3$. In other words, the absorption coefficient in this spectral region must be very large, while the corresponding absorption band must be very diffuse. This determines another specific feature of experimental studies of vibrational spectra of ferroelectric crystals. Namely, it becomes practically impossible to measure the IR absorption spectra, while the detection of such a band in the Raman spectra is transformed into a problem of extreme complexity.

The fundamental methods of studying vibrational spectra of crystals, which have already been in use for many years, are to measure the infrared absorption and Raman spectra of the crystals. Both of these methods are commonly used, since they can substantially supplement each other, in line with the fact that certain normal vibrations can be forbidden by selection rules in the infrared absorption spectra and allowed in the Raman spectra, and vice versa. We should note

that by using optical methods we can study only the optical branches of the normal vibrations, and only for values of the wave number $q \sim 0$.

Methods based on inelastic scattering of slow neutrons have recently become more and more promising. An important advantage of these methods is that they involve no selection rules forbidding the manifestation of particular normal vibrations of the crystals. In addition, neutron scattering permits one in principle to study experimentally the complete dispersion relations, both for the optical and acoustic branches of vibrations, and in particular, to get data on the vibration frequencies in the region $q \to 0$. The possibilities of these methods are not limited by considerations of principle, but rather, by the necessity of using large specimens and strong neutron fluxes to obtain the maximum intensity. The problem of the nature of the experimental data that one can get in the region $q \to 0$ using neutron scattering and the optical methods and the possibilities of interpreting them are discussed in [53]. We shall examine below the features of the experimental methods applicable in studying the vibrational spectra of ferroelectric crystals.

4.1. Methods of Infrared Spectroscopy and Raman Scattering

The first systematic studies of the large group of compounds having the perovskite structure were performed by measuring the transmission spectra in the near IR region at $300-1000$ cm^{-1}. They showed that these crystals are characterized by high absorption in the region of the normal vibrations, and that samples 1–3 microns thick are needed for practical measurements.[35, 36] Hence, the samples used have been thin single crystals or powder samples obtained by pressing a ground crystal of particle dimensions 1–5 microns with KBr powder or with polyethylene powder,[35, 44] or also by repeated deposition of the powder evaporated in air onto a KBr crystal substrate or onto a polyethylene substrate.[36, 42]

The reflection method has been the fundamental method in studies in the far infrared region, which is of greatest interest.[37-39, 42, 54] This is due to the fact that great dielectric dispersion is observed in this frequency region, as has been stated, and the thinnest specimens prove to be opaque. The specimen thickness was not of primary importance in using this method. The surfaces proved to be optically good enough in measurements of reflection from a natural face of a single crystal, and did not require preliminary polishing, as was necessary for polycrystalline specimens.[39, 42] An important merit of this method is that one can calculate the frequency-dependence of the refractive index and the absorption coefficient by mathematical treatment of the reflection-spectrum data. Hence, one can calculate the real and imaginary

parts of the dielectric constant over a large spectral range.

This method has been described in detail in [37, 38, 42, 54]. In brief, it is based on measuring the spectral variation of the coefficient of reflection $R(\omega)$ over a broad range of the spectrum, usually with normal incidence of the light beam on the crystal. Thus, at any point of the spectrum one finds the amplitude of the reflected wave $r(\omega) = \sqrt{R(\omega)}$. To find the second parameter, the phase $\phi(\omega)$ of the reflected wave, one uses the Kramers-Kronig relation, which relates these two quantities by way of an integral. Using known relations, one can easily calculate the optical parameters $n(\omega)$ and $k(\omega)$ for a given ω from the $r(\omega)$ and $\varphi(\omega)$ data, and also the real and imaginary parts $\epsilon'(\omega)$ and $\epsilon''(\omega)$ of the dielectric constant. Since the dispersion theory indicates that the frequency of the normal vibrations coincides with the maximum in the conductivity $\sigma(\omega)$, rather than in $\epsilon''(\omega)$, it is also useful to determine the variation of $\sigma(\omega)$. The Kramers-Kronig integral and all the stated parameters are usually calculated by electronic computers.[37, 38, 42, 54] In making this calculation, one replaces the integral over an infinite range with an integral over a fine range determined by the range of frequencies over which the reflection coefficient has been measured. In cases in which the region of measurements is not broad enough, some authors have extrapolated the experimental data. Here one has to make a special analysis of the sensitivity of the results of the calculation to the accuracy of such an extrapolation.[37, 38, 54] Use of the Kramers-Kronig analysis in the case of oblique incidence of the light beam on the specimen is discussed in the article.[55]

We should note that measurements in the far infrared (i.e., in the wavelength range from 50 to 1500 microns) have only recently been performed. This is explained by the fact that work in the far infrared is extremely difficult because of the low power of the radiation sources (heated black bodies). The problem of filtering the useful light from the much more intense short-wavelength radiation is also very complex in this spectral region. Laboratory spectrometers for the far infrared have been specially designed for such studies. They permit one to measure down to frequencies of ~ 10 cm^{-1} ($\lambda = 1000\,\mu$). Use of radio generators of microwave radiation (klystrons), together with the cited spectrometers, has extended the range of study to 1 cm^{-1}, using spatial separation of the higher harmonics of the radiation.[37, 47, 54]

Studies of the vibrational spectra of ferroelectric crystals by measuring Raman spectra are very difficult because the Raman lines of the most interesting "ferroelectric" vibrations should be very diffuse, and lie in the immediate vicinity of the exciting line. Hence, the studies of the Raman spectra of ferroelectric materials performed thus far have not yet

given as successful results as have been obtained by other methods. The method applied differs from the usual only in the care taken to eliminate stray light in the crystal and the instrument. In the given case, the stray light strongly masks the Raman spectrum, especially in the vicinity of the exciting line. Besides, as a rule, the high refractive index of ferroelectric crystals also greatly decreases the intensity of the Raman lines.

4.2. Methods Based on Inelastic Scattering of Slow Neutrons

As is known, the nature of the interaction of neutrons with matter depends essentially on their energy. Slow neutrons show great advantages in this regard over other forms of radiation, e.g., light, electrons, and x-rays, since the wavelength of such neutrons is comparable with the interatomic distances, while their energies are of the order of magnitude of the energies of the characteristic motions of atoms in solids and liquids (the vibrational and rotational motions of atoms and groups of atoms, diffusion, etc.), i.e., 0.1–0.001 eV.

Hence, on the one hand, slow neutrons can reveal the existence of order in the material being studied, as manifested in the coherence of the neutron scattering from different atoms. On the other hand, they can respond to any changes in the positions of atoms occurring during the time of effective interaction of the neutron with the atoms. In the latter case, in accordance with the uncertainty principle, the participation of the atoms in vibrational and diffusional motions must result in a change in the energy of the neutrons by the amount $\epsilon \sim \hbar/t$, where $t \sim 10^{-13}$–10^{-14} sec for optical vibrations in solids, and $t \sim 10^{-12}$ sec for diffusion in liquids like water. Hence, the change in the energy of the neutrons $\epsilon \sim 10^{-3}$–10^{-1} eV is of the same order of magnitude as the initial energy of the neutrons. Hence, it can easily be measured for each individual scattering event.

It is precisely these processes of inelastic scattering of slow neutrons accompanied by a change in their energy that provide information on the dynamics of the scattering medium. If we restrict ourselves to the case at hand of crystal-lattice vibrations of solids, it turns out, first, that neutrons are "active" with respect to all the lattice vibrations, in distinction from light and x-rays. These vibrations include all those, both optical and acoustic, with arbitrary q vectors, that can be represented as plane waves of the type of (1, 3). Second, only neutrons permit one to get experimentally complete dispersion laws $\omega = \omega_s(q)$ for all s branches of the vibrational spectrum of lattice frequencies.

The reader can find a systematic presentation of all the problems of the theory of interaction of slow

neutrons with matter and of the possibilities emerging from the theory of experimentally studying the dynamics of condensed systems in the books of Turchin[56] and of Gurevich and Tarasov.[57] The problems of methodology of the corresponding neutron experiments are thoroughly treated in the review of Brockhouse et al.[58-60] Here we shall summarize with reference to these sources some information on inelastic scattering of slow neutrons, as is necessary for understanding the results of the studies presented below.

In a neutron experiment, one usually gets data on the second-derivative scattering cross-section $\partial^2\sigma/\partial\Omega\partial\epsilon$. This determines the probability that a neutron scattered in the given range of solid angle between Ω and $\Omega + d\Omega$ will have an energy within the range between E and E + dϵ. The experimental methods used for these purposes make it possible to record in one or several directions the relation between the intensity of the scattered neutrons and their energy change, as compared with a fixed initial or final energy value assigned by the experimenter. Here one can get all the data necessary to construct the dispersion curves $\omega = \omega_s(q)$ from the experimental results on inelastic coherent scattering from single crystals. For simple enough crystal structures, one can get the real frequency distribution function $g(\omega)$ (the phonon spectrum) from experimental data on inelastic incoherent scattering of neutrons by polycrystals. One can then compare the phonon spectrum with various theoretical models of atomic interactions defining the features of the dynamics of the material being studied.

The nature of the variation of the neutron energy caused by interaction with lattice-vibration quanta (phonons) depends substantially on the experimental conditions. Depending on the initial energy of the neutrons and the nature and temperature of the material, a neutron can transfer part of its energy to excite vibrations (one says that the neutron generates phonons) or, conversely, it can gain extra energy from the energy of the lattice vibrations (in this case one says that the neutron absorbs phonons).

The laws of conservation of energy and momentum of the neutrons hold true in the following form for inelastic coherent scattering of neutrons with absorption or generation of phonons:

$$E - E_0 = \frac{\hbar^2}{2m}(k^2 - k_0^2) = \mp \hbar \sum_{i=1}^{m} \omega_i, \qquad (4.1)$$

$$k - k_0 = 2\pi\tau \mp \sum_{i=1}^{m} q_i, \qquad (4.2)$$

Here E_0, k_0, and E, k are the energy and momentum values of the neutron before and after scattering, respectively. ω_i and q_i are the frequency and wave vector of the i-th phonon participating in the scattering process, τ is an arbitrary reciprocal-lattice vector, and the − and + signs refer respectively to the processes of generation and absorption of individual phonons.

At not too high temperatures, not exceeding the Debye temperature of the crystal being studied, scattering with generation or absorption of a single phonon (m = 1) predominates. The role of many-phonon processes increases greatly with rising temperature, and the interpretation of them is very difficult. Without discussing this problem further, we shall only mention that the spectrum of the neutrons scattered in many-phonon processes is continuous, in distinction from single-phonon processes. This fact makes it possible qualitatively to distinguish the interfering contribution from many-phonon processes in interpreting the features of single-phonon scattering.

The laws of conservation of momentum (4.2) in single-phonon scattering imply that in scattering the neutron transfers part of the momentum $\hbar q$ to the phonon, or receives it from the latter. The other fraction $\hbar \cdot 2\pi\tau$ of the momentum defines the participation in the scattering process of the crystal as a whole without energy transfer. This case where $k - k_0 = 2\pi\tau$ is shown schematically in Fig. 8a. It corresponds to elastic coherent scattering, on which the classical methods of neutron and x-ray diffraction are based. Figs. 8b and c show on the same scale the vector diagrams corresponding to the cases of inelastic coherent scattering with generation or absorption of a phonon.

For a given k_0, let us bear in mind the fact that $k = k\Omega$ for scattering in the direction defined by the unit vector Ω. Then the conditions (4.1) and (4.2) are two equations for the single unknown k, and they can have only a finite number of solutions. Thus, the spectrum of the neutrons inelastically and coherently scattered in a certain direction is discrete, and it has the form of rather sharp maxima on the background of the continuous contributions from incoherent and many-phonon scattering.

Each of these maxima for a given k_0 and a given scattering geometry (i.e., the scattering direction Ω is given) determines a pair of values of ω and q. By measuring the spectra under various conditions ensuring the satisfaction of the conditions (4.1, 4.2) for
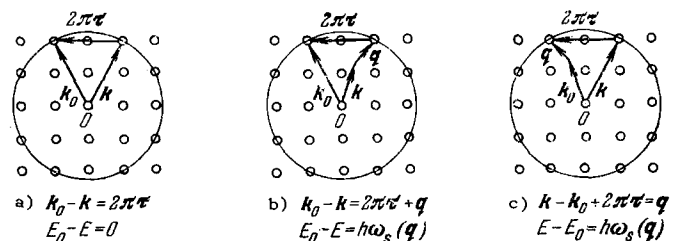

FIG. 8. Laws of conservation of momentum in reciprocal space in elastic and inelastic neutron scattering: a) elastic coherent scattering, b) inelastic scattering producing phonons, c) inelastic coherent scattering absorbing phonons.

various values of the energy and momentum transfers, we can obtain a set of values of ω and $\mathbf{q}$ adequate to construct the complete dispersion curves $\omega = \omega_S(\mathbf{q})$.

In proceeding to consider the information that we can get from inelastic incoherent neutron scattering, we shall note first of all that the conditions of conservation of quasimomentum in the form (4.2) are not fulfilled in this case. This is because the crystal as a whole takes up the entire change in the neutron momentum $\hbar(\mathbf{k} - \mathbf{k}_0)$, in spite of the participation of elementary excitations (phonons) in the scattering process. Consequently it turns out that the spectrum of the inelastically and incoherently scattered neutrons is continuous, in distinction from the coherent scattering. However, certain features of the continuous spectra of inelastic neutron scattering can be correlated with concrete lattice vibrations. The possibility of such a correlation is based on the fact that maxima in the scattered-neutron intensity must occur in the frequency region having greatest statistical weight in the phonon spectrum of the substance being studied. From this standpoint, those branches of the phonon spectrum whose dispersion curves $\omega_S = \omega_S(\mathbf{q})$ are characterized by small values of $d\omega/d\mathbf{q}$ over a rather broad range of $\mathbf{q}$ values should make a substantial contribution to the neutron scattering. Evidently, "flat" optical branches satisfy these conditions, as well as "flat" regions of the acoustic branches in the region of $\mathbf{q}$ values near a Brillouin zone boundary (see Fig. 21 for $SrTiO_3$). That is, the conditions are fitted by all the regions of the acoustic and optical branches within which a great enough number of vibrations having different $\mathbf{q}$ values occur within a narrow enough range of frequencies.

Here a fraction of the peaks in the neutron spectrum due to sufficiently flat transverse optical branches of vibrations having different $\mathbf{q}$ values must lie in the frequency region obtainable from infrared and Raman spectra for $q \sim 0$. This also implies that the contribution to the neutron spectrum from the most interesting low-frequency optical branch must be distributed over a larger range of frequencies, owing to its anomalous behavior at small $\mathbf{q}$. Hence, it is harder to distinguish unequivocally in the total scattering pattern. The correlation with infrared data for this branch becomes correspondingly indefinite.

5. RESULTS OF EXPERIMENTAL STUDY OF CRYSTAL LATTICE DYNAMICS OF FERRO-ELECTRIC SUBSTANCES

The fundamental conclusions of the dynamic approach to the theory of ferroelectricity presented in Secs. 1 and 2, which can be verified experimentally, are:

1. The conclusion that dispersion expressions like (3) and relations like (1.22), which were derived for classical ionic crystals, can be applied to describe the dielectric properties of ferroelectric substances of the $BaTiO_3$ type.

2. The conclusion that the vibrational spectrum of ferroelectric crystals should contain a "soft ferroelectric" vibration belonging to one of the transverse optical branches, and characterized by a low resonance frequency and high anharmonicity. This vibration must be mainly responsible for the high value of the low-frequency dielectric constant of such crystals.

3. The fundamental conclusion of the theory that such a vibration in ferroelectric crystals should show a high temperature-dependence, with a frequency that declines anomalously according to the law $\omega_T \sim (T - T_C)^{1/2}$ as the temperature approaches a first-order phase-transition point, and generally approaches zero as the temperature approaches the phase-transition point in crystals possessing a second-order phase transition.

4. The conclusion that fluctuations increase appreciably under certain conditions in the phase-transition region, and that they enhance the intensity of the Raman line involved in the ferroelectric transition.

We considered in Sec. 3 which vibrations we should expect in the spectrum of the ferroelectric crystals of greatest interest to us, having the perovskite structure (e.g., $BaTiO_3$). Now we shall take up a detailed analysis of the results of experimental study of the crystal-lattice dynamics of ferroelectric materials, i.e., study of the features of their vibrational spectra and the temperature-dependence of the frequency and form of the vibrational bands in the phase-transition region.

5.1. Infrared Spectra

Studies of vibrational spectra of ferroelectric crystals by infrared spectroscopic methods began rather long ago. However, at first they were individual and disconnected in nature. In 1957, Last[35] carried out the first systematic study of a large group of compounds having perovskite-type crystal structures, including $BaTiO_3$. Since suitable apparatus did not exist at that time, the range of studies was restricted to the near infrared (300–1000 cm^{-1}). That is, it did not include the very interesting long-wavelength infrared range. According to Last, the transmission spectra of powdered samples (obtained by pressing in KBr) of a large group of perovskite-type crystals showed two bands having minima in the regions 500–600 cm^{-1} and 350–400 cm^{-1} (Fig. 9). Similar measurements on single crystals were carried only to 400 cm^{-1}, owing to insufficient intensity of radiation in the longer-wavelength region of the spectrum. Here he also found a band at ~ 500 cm^{-1}. However, it turned out that the absorption rapidly increased with further increase in wavelength, and hence, the second band at lower frequency was not observed. Last ascribed the two ob-
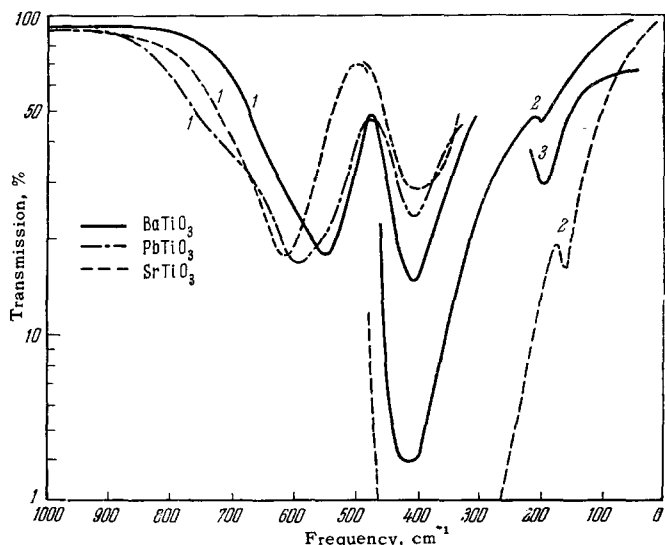
FIG. 9. Transmission spectra of powdered $SrTiO_3$, $PbTiO_3$, and $BaTiO_3$. 1 — [35], 2 — [42], 3 — [44].

FIG. 10. Temperature-variation of the bands in the absorption spectrum of $BaTiO_3$ in the vicinity of 500 cm^{-1}.[35]

served absorption bands respectively to the internal stretching and deformation vibrations of type F_{1u} of the TiO_6 octahedron. Naturally, Last could not observe the most interesting third F_{1u}-type infrared-active vibration at lowest frequency. The transmission spectrum of tetragonal $BaTiO_3$ showed no essential changes when the temperature was dropped below the phase-transition point $\theta = 120°$ C. The orthorhombic $BaTiO_3$ crystal showed a splitting of the high-frequency band. In accord with the data of Sec. 3, this apparently involves the change in the symmetry of the crystal and partial removal of the degeneracy of the vibrations (Fig. 10). Thus, no anomalous changes in the vibrational spectrum were found in near-infrared studies in the region of the phase transition of $BaTiO_3$. Other investigators have subsequently carried out similar measurements. Together with the cited absorption bands, they observed some other absorption bands at higher frequencies, e.g., near 1250 and 1000 cm^{-1} for $BaTiO_3$. These should evidently be interpreted as manifesting derived harmonics of the fundamental vibrations.[36, 44]

Research in the far infrared has contributed substantially to the study of the vibrational spectra of perovskite-type crystals. The first measurements of the transmission and reflection spectra over the broad infrared range 10,000–10 cm^{-1} were performed by Barker[37] and Ikegami[39] on single crystals of $SrTiO_3$ and $BaTiO_3$, and on polycrystalline specimens of $SrTiO_3$, $BaTiO_3$, and $CaTiO_3$ by Ikegami, Murzin, Demeshina, Stekhanov, et al.[39, 42-44] Spitzer et al.[38] have studied in detail single crystals of $SrTiO_3$ and $BaTiO_3$ in the spectral range 10,000–70 cm^{-1}.

In measuring the transmission spectra of powder layers and the reflection spectra of the stated crystals, they observed in these studies a new vibration occurring in the region 170–180 cm^{-1} (Figs. 9 and 12).

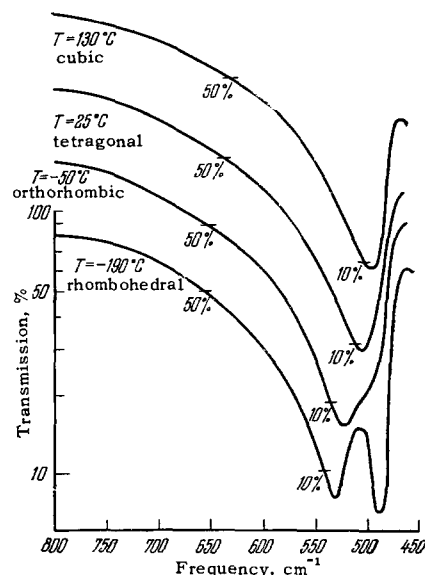According to the data of [39, 42], it underwent no substantial changes as the temperature approached the ferroelectric phase-transition point of $BaTiO_3$ ($\theta = 120°C$). Therefore, it was not the "ferroelectric" vibration. On the other hand, a special study of the infrared absorption spectra in the vicinity of 400 cm^{-1}, where all the $BaTiO_3$-type crystals showed a transmission minimum in the powder state, showed that: first, this minimum strongly depends on the dimensions of the powder particles, and second, it is not observed in the transmission spectra of even the thinnest single crystals of $SrTiO_3$ and $BaTiO_3$.[37, 38, 54] In addition, estimates showed that the existence of a vibration at ~400 cm^{-1} having an oscillator strength even ten times as small as that of the 550-cm^{-1} vibration would produce a detectable trough in the reflection curve. This was not observed experimentally.[61] Hence, most investigators have concluded that the transmission minimum of $BaTiO_3$-type materials in the powder state in the vicinity of ~400 cm^{-1} is not due to any vibration, but must be explained by scattering of the infrared radiation by the particles of the powder, since the refractive index of the crystals increases greatly in this region of the spectrum.*

The fundamental results in the study of the vibrational spectra of the stated crystals have been obtained

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*We should mention here the study [44], according to which the transmission spectra of powder specimens of $BaTiO_3$ and $PbTiO_3$ pressed in polyethylene tablets also showed the three previously noted bands in the frequency ranges 170, 300–400, and 500–600 cm^{-1}. However, in this case, the two high-frequency bands had a triplet structure. This feature of the absorption spectra of $BaTiO_3$ and $PbTiO_3$ crystals hardly agrees with the data of other investigators. Apparently, it requires further measurements, above all, to establish more exactly the effect of the matrix material of the specimens, etc.
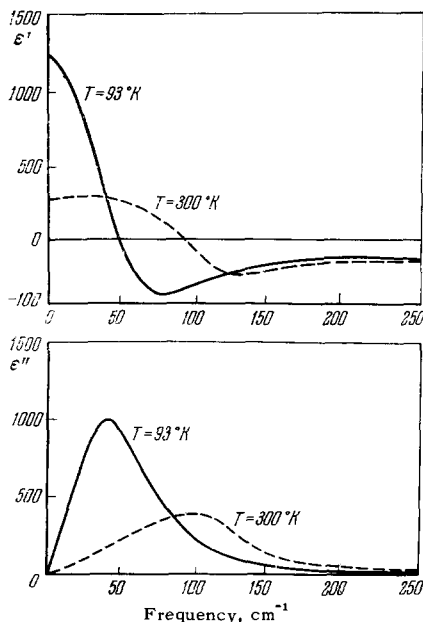
FIG. 11. Temperature-variation of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ for monocrystalline SrTiO$_3$.[37]

by measuring reflection spectra over a broad range of the infrared, with subsequent mathematical treatment by the above-described method using the Kramers-Kronig relation and numerical integration by computers.[37, 38, 42, 54] One of the first of such studies was that of Barker and Tinkham.[37] They measured the reflection spectrum of single crystals of SrTiO$_3$ over the range 2.5–3000 cm^{-1}. After mathematical treatment, they found all three absorption bands expected in the infrared spectra, corresponding to the three F_{1u}-type vibrations whose resonance frequencies at room temperature proved to be 550, 175, and 100 cm^{-1}.*

Thus the vibration of lowest frequency was first discovered in the infrared spectra of BaTiO$_3$ crystals in the vicinity of 100 cm^{-1}. These vibrations were correspondingly interpreted (following Last) the first two as the internal vibrations of the TiO$_6$ octahedron, and the lowest-frequency vibration as the motion of the Sr cation with respect to the TiO$_3$ group. The most essential result of [37] was that they were the first to detect the anomalous temperature-dependence of the frequency of the low-frequency vibration of SrTiO$_3$ by analyzing the reflection spectra of SrTiO$_3$ obtained at 300° K and 93° K (Fig. 11). Upon going from 300° K to 93° K, the frequency of this vibration varied from 100 cm^{-1} to 50 cm^{-1}, i.e., by a factor of two. Since here the low-frequency dielectric constant increased approximately by a factor of four, this also indicates that relations like (3) and (1.22) hold for SrTiO$_3$. Thus,

the result of this study agrees qualitatively with the conclusions of the dynamic theory of ferroelectric crystals, and can be considered to be its first qualitative confirmation.

Spitzer et al.[38] have made a detailed analysis of the reflection spectra of single crystals of BaTiO$_3$, SrTiO$_3$, and TiO$_2$, both by using the Kramers-Kronig relation and on the basis of the dispersion theory. Fig. 12 shows the experimental relationships R(ω) over the frequency range from 5000 to 70 cm^{-1}. The $\epsilon''(\omega)$ variations calculated on this basis for BaTiO$_3$ and SrTiO$_3$ (Fig. 13) are analogous in form, and also indicate the existence of three resonances in the regions of 500, 180, and below 100 cm^{-1}. They approximated the relation $\epsilon''(\omega)$ and the variation of R(ω) by using three damped oscillators on the basis of dispersion theory. This made it possible to obtain the dispersion parameters of these oscillators given in Table II best fitting the experimental data. The reflection curves obtained from the dispersion theory are shown in Fig. 12 by the solid lines. We see that these curves generally agree very well with the experimental data, except in the region around 330 cm^{-1}. It was later shown that this discrepancy can be explained by the effect of phonon-phonon interaction. Taking account of the latter gave good enough agreement of the theoretical and experimental $\epsilon'(\omega)$ and $\epsilon''(\omega)$ curves and the reflection spectra.[61] The peculiarity of the $\epsilon''(\omega)$ curve for BaTiO$_3$ in this study is the fact that the low-frequency resonance proved to be outside the limits of the frequency range over which the R(ω) data were measured, i.e., in the region of extrapolation of the R(ω) values to the value R$_0$ = 0.914, as calculated from ϵ_0 = 2000.

In [42, 43], they determined the reflection spectra of BaTiO$_3$, SrTiO$_3$, and a number of other compounds from polycrystalline specimens, and subjected them to the described mathematical treatment. They measured them over the range 10–5000 cm^{-1}, and at discrete points down to 1.25 cm^{-1}, i.e., in a spectral range encompassing all three resonance vibrations of perovskite crystals. The values of the resonance frequencies, damping constants, and oscillator strengths of the three resonances determined according to the dispersion formulas from the calculated variations of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ generally agree with the analogous data of other investigators (see Table II). We should point out that the frequency of the lowest-frequency vibration for polycrystalline BaTiO$_3$ is approximately two times that for a monocrystalline specimen. However, this does not involve a difference in the internal properties of the crystals, but is a natural consequence of the fact that the measured dielectric constant and reflection coefficient for polycrystalline specimens are always considerably lower in absolute magnitude. This has a considerable effect in calculating $\epsilon(\omega)$, particularly in the low-frequency region.

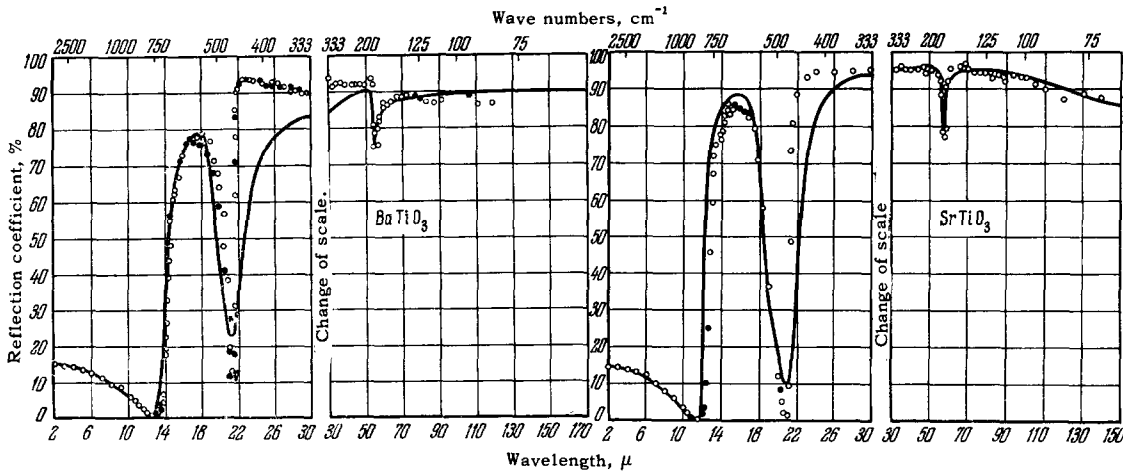The temperature-dependence of the reflection spec-

*The 175-cm^{-1} vibration is not shown in the diagrams, since it was noted only in supplementary measurements made after it had been pointed out by Spitzer et al. [38] Barker [37] has remarked on this in the form of a note added in proof.

Wave numbers, cm^{-1}

FIG. 12. Reflection spectra of single crystals of BaTiO$_3$ and SrTiO$_3$.[38]

Table II. Parameters of the dispersion oscillators of SrTiO$_3$ and BaTiO$_3$ of the form

$$\epsilon(\omega) = \epsilon_\infty + \sum_i (4\pi a_i \omega_i^2)/\omega_i^2 - \omega^2 + i\gamma_i\omega_i\omega)$$

		SrTiO$_3$ (monocryst.)[38]		SrTiO$_3$ (polycryst.)[42]		BaTiO$_3$ (monocryst.)[38]		BaTiO$_3$ (polycryst.)[42]	
λ_1	ω_1	18.2 μ	456 cm^{-1}	17.9 μ	558 cm^{-1}	19,6 μ	510 cm^{-1}	19,7 μ	508 cm^{-1}
	$4\pi a_1$	1,9		1.0		1,0		1,0	
	γ_1	0,049		0.09		0,057		0,095	
λ_2	ω_2	56.3 μ	178 cm^{-1}	60 μ	167 cm^{-1}	54,7 μ	183 cm^{-1}	55 μ	182 cm^{-1}
	$4\pi a_2$	3,6		—		2,0		—	
	γ_2	0,034		—		0.031		—	
λ_3	ω_3	114 μ	87.5 cm^{-1}	102 μ	98 cm^{-1}	296 μ	33.8 cm^{-1}	139 μ	72 cm^{-1}
	$4\pi a_3$	299,3		175		2000		455	
	γ_3	0,3		0.73		2.5		2.2	

tra of SrTiO$_3$ and BaTiO$_3$ was studied in the range 45−140°C in the cited reference.[42] While no appreciable changes were observed for SrTiO$_3$, as we should expect, the spectra of BaTiO$_3$ showed a marked increase in the reflection at the long-wavelength limit of the 10−30 cm^{-1} infrared region as the temperature approached the phase-transition point (Fig. 14). The frequency-dependence of the complex dielectric constant of BaTiO$_3$ calculated from these experimental data for different temperatures is shown in Fig. 15. It distinctly demonstrates the variation of the low-frequency vibration of BaTiO$_3$ (Table III). We see that as the temperature approaches the phase-transition point, the frequency of this vibration decreases considerably, approximately following the theoretical law $\omega_3^{theor} = A(T - T_C)^{1/2}$. This is accompanied by an in-

crease in its oscillator strength and degree of anharmonicity. We also see from Table III that the damping constant, and hence also the degree of anharmonicity, of this vibration increase hereby by a factor of more than three. The lowest experimental value ($\sim$ 33 cm^{-1}) of the frequency of the lowest-frequency vibration near the phase-transition point was compared with the theoretical value $\sim$ 19 cm^{-1}. The latter was estimated by Ginzburg's[9] theory using Eq. (5), in which $\alpha'_{\theta_{meas}} = 9 \times 10^{-5}$, $\theta_{meas} = 112°C$, $T_{C_{meas}} = 125°C$, and μ is the reduced mass of this vibration, which was handled approximately in the form Ba−TiO$_3$ or BaO$_2$−TiO. We can consider the comparison quite satisfactory.

Special attention was paid in [37, 38, 42] to two features of the vibrational spectrum of perovskite-type
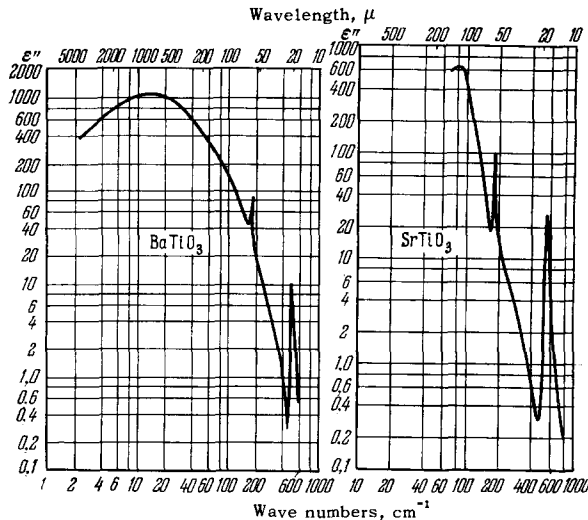
FIG. 13. Spectral variation of $\epsilon''(\omega)$ for BaTiO$_3$ and SrTiO$_3$ calculated from the data of Fig. 12.[38]

FIG. 15. Temperature-variation of the $\epsilon'(\omega)$ and $\epsilon''(\omega)$ curves for polycrystalline BaTiO$_3$.[42] 1 — 45°C, 2 — 80°C, 3 — 110°C, 4 — 140°C.

crystals, in particular, the extremely large oscillator strength and the high degree of anharmonicity of the lowest-frequency vibration, which determines more than 90% of the entire polarization of the BaTiO$_3$ crystal. These features were analyzed in detail in [42]. Using Cochran's[10] method, an explicit dispersion expression was derived for the complex dielectric constant of perovskite-type crystals in the cubic phase. By comparing this expression with the experimentally-determined values of the dispersion parameters of the vibrations of BaTiO$_3$ (see Table II) for a concrete model of the normal vibrations, it was possible to estimate a number of the microscopic characteristics of the BaTiO$_3$ crystal: the displacements of the ions in the different normal vibrations as a function of the external fields; the total polarizability of the unit cell and the component of it due directly to displacement of the ions; the magnitude of the local electric fields as a function of the external electric field and the ionic charges; and the ionic polarizability of the atoms of the crystal.

The obtained results qualitatively agree with independent calculations of the internal fields and polarization for the static model of BaTiO$_3$.[62] The very interesting conclusion was drawn from these estimates
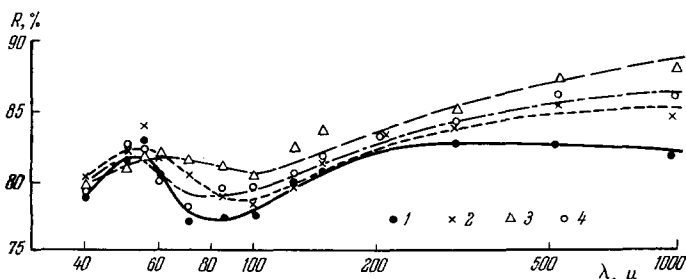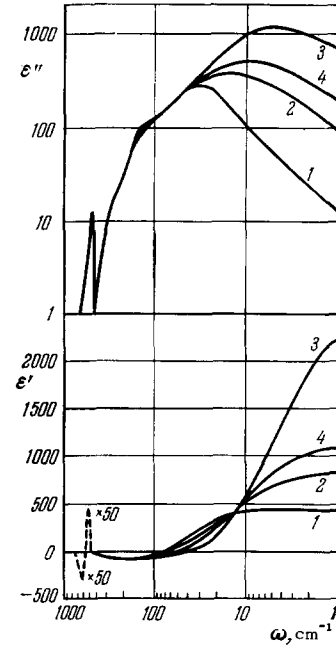
that the electronic polarization of the ions makes the major contribution to the overall polarization (65–80%). As regards polarization, this indicates that the highest-frequency "ferroelectric" vibration of BaTiO$_3$-type crystals has a complex electronic-ionic nature (see Sec. 1.1d).

Similar measurements at different temperatures in the range from 24° to 200° C, and in the range 1–1000 cm^{-1} were later performed also on single crystals of BaTiO$_3$.[54,105] The vibrational spectrum of monocrystalline BaTiO$_3$ was determined by using the above-described mathematical treatment of the reflection spectra of BaTiO$_3$. It also consists of three vibrations, at 491, 182, and 88 cm^{-1} (T = 200° C). When the crystal transformed from the cubic to the tetragonal phase, the reflection spectra showed a splitting of the 182-cm^{-1} vibration into two, having frequencies of 182 and 174 cm^{-1} at 100° C (Fig. 16). This agrees with the conclusions from symmetry theory (see Sec. 3). When the temperature was raised above the phase-transition point, a spectral shift was

FIG. 14. Temperature-variation of the reflection spectrum of polycrystalline BaTiO$_3$.[42] 1 — 45°C, 2 — 80°C, 3 — 110°C, 4 — 140°C.

Table III. Temperature-variation of the dispersion parameters of the low-frequency vibration of BaTiO$_3$

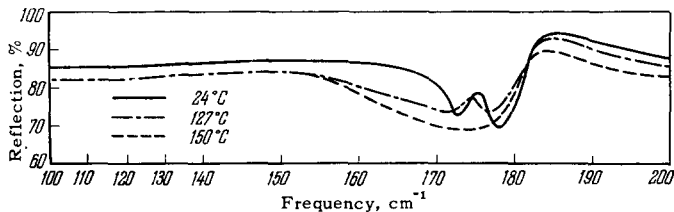| T, °C	45° C	80° C	100° C	110° C	140° C
ω_3	72 cm^{-1}	65 cm^{-1}	47 cm^{-1}	33 cm^{-1}	58 cm^{-1}
$4\pi a_3$	455	900	1500	2500	1200
γ_3	2.2	4.2	5.2	7.0	5.0
ω_3^{theor}	72 cm^{-1}	52 cm^{-1}	40 cm^{-1}	31 cm^{-1}	57 cm^{-1}

FIG. 16. Temperature-variation of the reflection spectra of BaTiO$_3$ in the vicinity of 180 cm^{-1}.[54]

observed in the frequency of the maximum of $\epsilon''(\omega)$ and the resonance frequency of the low-frequency vibration of BaTiO$_3$, as determined from the position of the maximum of $\sigma(\omega)$(Fig. 17 and Table IV). This agrees qualitatively with the predictions of the dynamic theory. The fact that the values of the frequency of this vibration were lower than Cochran's estimates is explained by noting that Cochran's theory does not take into account the great anharmonicity of this vibration.

Thus, most investigators think that the vibrational spectrum of crystals having perovskite-type structures consists of three F_{1u}-type vibrations having frequencies $\omega_1 \sim 550-600$ cm^{-1}, $\omega_2 \sim 170-180$ cm^{-1}, and $\omega_3 \sim 30-90$ cm^{-1}. BaTiO$_3$ shows a splitting of the 550 and 175^{-1} bands with decreasing temperature. This apparently involves the change in symmetry of the crystal. Here the 175-cm^{-1} vibration splits in the tetragonal phase, but the 550-cm^{-1} vibration only in the orthorhombic phase. Analysis of the experimental data has shown that dispersion theory with account taken of phonon-phonon interaction describes rather well the frequency-dependence of the reflection coefficient of crystals having perovskite-type structures (SrTiO$_3$, BaTiO$_3$). Minor deviations can be explained by noting that the damping constant was considered to be frequency-independent in the applied dispersion analysis. However, this is not true even for simple alkali-halide crystals.[63] Another outcome of the described infrared studies is that the vibrational spectrum of perovskite-type crystals shows a "soft" ω_3 vibration distinguished by low frequency and high anharmonicity, and giving rise to a great dispersion in the dielectric constant. This vibration is responsible
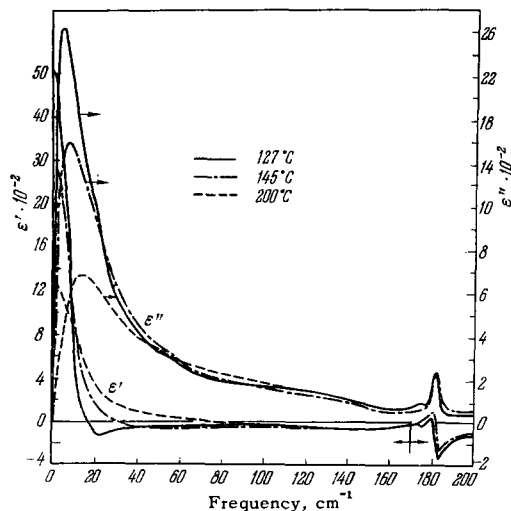
FIG. 17. Temperature-variation of the $\epsilon'(\omega)$ and $\epsilon''(\omega)$ curves for a single crystal of BaTiO$_3$.[54]

for more than 90% of the polarization of crystals of this type, and shows the most anomalous parameters in the case of BaTiO$_3$.

Finally, studies of the temperature-variation of the infrared reflection spectra of SrTiO$_3$ and BaTiO$_3$ crystals have resulted in the first detection and analysis of the phenomenon of variation of the frequency and other parameters of the "soft ferroelectric" vibration in the vicinity of the phase transition. The experimental data proved to agree satisfactorily with theoretical relationships of the type of (1.19). This apparently indicates that the same expressions of the dynamic theory can be applied to crystals of the BaTiO$_3$ type as are used in describing classical ionic crystals. Thus, these studies were the first test and confirmation of the dynamic theory of ferroelectricity described in Sec. 1.

A number of studies have also recently appeared on the vibrational spectra of certain ferroelectric crystals having more complex structures, in particular, hydrogen-bonded ferroelectric substances like KH$_2$PO$_4$ and triglycine sulfate, which show a piezoeffect in the paraelectric region. Generally speaking, as was noted in Sec. 1, Cochran's[111] theory of these crystals is fundamentally qualitative in nature, and at present is not supported by experimental facts that could be interpreted with sufficient definiteness.

Prior study had been made of the spectra of these crystals.[64, 69] However, the measurements had been limited to the near infrared alone. Hence, the interesting low-frequency "ferroelectric" vibration was omitted from consideration. Barker and Tinkham[70] and Bazhulin, Aref'ev et al.[711] have studied these crystals over a broad range of the infrared, including the far infrared. Barker measured the reflection spectrum of both crystals over the range 2.5 – 1500 cm^{-1} at different temperatures, and then by mathematical treatment determined the spectral vari-

Table IV.

T, °C	ω_3, cm^{-1}	ω_2, cm^{-1}		ω_3, cm^{-1}	Position of the corresponding maximum of $\epsilon'(\omega)$, cm^{-1}
24	491±1	182±1	174±1	41	12^{+4}_{-2}
100	491±1	182±1	174±1	—	22±10
127	491±1	182±1	—	13	6^{+7}_{-1}
145	491±1	182±1	—	26	8^{+6}_{-2}
200	491±1	182±1	—	88	13±4
115 *)	491±1	182±1	174±1	—	39±20

*Crystal partially depolarized.

ation of $\epsilon'(\omega)$ and $\epsilon''(\omega)$. As a result, in addition to a series of lines corresponding to the normal vibrations of the crystals, which varied slightly upon passing through the phase-transition point, KH_2PO_4 showed a highly diffuse band in $\epsilon''(\omega)$ in the region $10-100$ cm^{-1}. The peak of the latter shifted appreciably in the spectrum upon approaching the phase-transition point. The frequency of the maximum of $\epsilon''(\omega)$ in the phase-transition region ($\theta = 123°$ K) was ~ 2.5 cm^{-1}. Thus, we can naturally consider this particular vibration to be responsible for the ferroelectric properties of KH_2PO_4. They couldn't find such a band for the triglycine sulfate crystal, and the authors assume from the shape of the $\epsilon''(\omega)$ curve that the maximum of the band apparently lies at frequencies below 14 cm^{-1}. Since the absorption bands of the cited crystals are very broadened, the authors concluded that, in distinction from perovskite-type crystals, the classical theory of damped oscillators characterized by a resonance frequency and a damping constant can't be applied to hydrogen-bonded ferroelectric substances. Rather, the hypothesis was advanced here that KH_2PO_4 and triglycine sulfate crystals undergo an order-disorder phase transition (see also [100, 104]). Aref'ev et al.[71] studied the transmission spectrum of powdered KH_2PO_4 pressed in paraffin tablets. The measurements were made over the spectral range $20-235$ cm^{-1} at temperatures $150-300°$ K. Along with bands at higher frequencies, the spectrum at room temperature showed a broad, intense absorption band with a maximum at 52 cm^{-1}. As the temperature was lowered toward the phase-transition point, it was appreciably shifted toward lower frequencies (42 cm^{-1} at T = 150° K; we recall that $\theta = 123°$ K), and it broadened considerably. Thus, these measurements made it possible to observe directly a "soft" vibration that could apparently be related to the ferroelectric properties of KH_2PO_4. However, the nature of the ferroelectricity in this type of crystals is very complex, and further studies are needed in order to interpret the obtained results.[72-74]

5.2. Raman Spectra

As was stated, Ginzburg and Levanyuk[28-30] showed that ferroelectric crystals near the phase-transition point should show a change in the spectral composition of the scattered light. In particular, the Raman line corresponding to the "ferroelectric" vibration should shift toward the exciting line as the temperature approaches the phase-transition point, and we should observe a considerable increase in its intensity.

Apparently, experimental studies[75-76] on the Raman spectra of quartz on passing through the phase-transition point at 575° C confirm this theory. One of the low-frequency Raman lines in the spectrum of quartz (207 cm^{-1}) was strongly shifted with increasing

temperature toward the exciting line (by more than 40 cm^{-1}[175]), and became much more diffuse. It completely disappeared from the spectrum above the phase-transition point. In addition, the marked increase in the intensity of scattered light and the appearance of "critical opalescence" observed in the phase-transition region in these crystals[77] agree well with the predictions of Ginzburg's theory.

The first attempts at directed study of the vibrational spectra of ferroelectric materials by the Raman method were made on the perovskite-type crystals $SrTiO_3$ and $BaTiO_3$.[40, 52, 78] However, owing to great experimental difficulties, these measurements were performed at only one temperature, 20° C. Under these conditions $SrTiO_3$ has a cubic structure, while $BaTiO_3$ is tetragonal. In essence, the vibrational spectrum for $SrTiO_3$ was observed over a wide range of frequencies for the first time.[40] The Raman spectrum of $SrTiO_3$ consisted of four lines with maxima at 620, 447, 335, and 90 cm^{-1}. The bands found at 620, 336, and 90 cm^{-1} were assigned respectively to the three F_{1u}-type vibrations ω_1, ω_2, and ω_3 discussed above. The 447-cm^{-1} band was erroneously assigned to another F_{1u}-type vibration, which was interpreted as a rotational vibration of the oxygen octahedron about the Sr–Ti axis. In general, as was shown in Sec. 3, consideration of the symmetry properties of cubic crystals having perovskite-type structures (including $SrTiO_3$) implies that in this case one should not observe a first-order Raman spectrum at all, since it is forbidden by the selection rules. The very fact that it is observed led the authors to conclude that $SrTiO_3$ shows considerable internal distortions of the cubic structure, and the selection rules are violated.

The studies of $BaTiO_3$ have proved to be less successful. The Raman spectrum showed only high-frequency vibrations. According to the data of Bobovich et al.,[52] the Raman spectrum of monocrystalline $BaTiO_3$ consisted of three lines with maxima at 695, 550, and 500 cm^{-1}. They interpreted the obtained results on the basis of a not very accurate analysis of the symmetry properties of this crystal. Ikegami has obtained a more complete Raman spectrum of single crystals of $BaTiO_3$ prepared by a cleaner method, using the relatively long-wavelength exciting line (5461 Å) from a mercury lamp.[78] The Raman spectrum of $BaTiO_3$ showed seven lines at frequencies 1181, 823, 736, 513, 502, 416, and 359 cm^{-1}. He made a detailed comparison of these data with the results of other studies, and interpreted them. According to the theoretical analysis (Sec. 3), the Raman spectrum of tetragonal $BaTiO_3$ should consist of eight vibrations, of symmetry types: $3 A + 1 B_1 + 4 E$. Correspondingly, the 513 and 502 cm^{-1} vibrations were considered to be the two highest-frequency vibrations of the types ω_1' and ω_1''. The 359-cm^{-1} vibration was considered to be one of the components of the lowest-frequency ω_3

vibration, and 416 cm^{-1} was assigned to one of the components of the ω_4 vibration. The high-frequency Raman lines at 736, 823, and 1181 cm^{-1} were interpreted simply as second harmonics of the cited vibrations at 359, 416, and 513 cm^{-1}. Thus, while not taking time to interpret each Raman line concretely, which undoubtedly would require further special studies, we must acknowledge the agreement between the infrared and Raman spectra to be satisfactory.

Recently Perry and Hall[97] have published a note reporting a study of the Raman spectra of single-crystal $BaTiO_3$ at various temperatures in the range 4–475° K. The following lines were observed in the study at 290° K, and taking their interpretation into account, we can write them in the form $\omega_1(LO)$ = 722 cm^{-1}, $\omega_1(TO)$ = 518 cm^{-1}, $\omega_4(LO, TO)$ = 307 cm^{-1}, and $\omega_3(LO)$ = 271 cm^{-1}. Here LO and TO denote, as usual, the longitudinal and transverse optical vibrations. As the temperature was lowered and the specimen passed through the orthorhombic and rhombohedral phases, a new band was found to appear: $\omega_2(TO)$ = 195^{-1}. Then both it and the $\omega_1(TO)$ band split in two. However, it seems that the most interesting fact was that the frequency of the line $\omega_3(LO)$ was found to be strongly temperature-dependent. This line shifted from 271 cm^{-1} (T = 290° K) to 230 cm^{-1} (T = 408° K). This was the particular reason for interpreting it as the longitudinal vibration of type $\omega_3(LO)$, which has a certain relation to the "ferroelectric" vibration $\omega_3(TO)$ (see Sec. 1.1c).

As we have stated, it is very difficult to study substances having perovskite-type structures by the Raman method because of the complications of preparing transparent enough crystals. Hence, the Raman method has been applied more widely in studying the vibrational spectra of certain other crystals whose preparation involves less difficulty.

Bazhulin, Stekhanov, et al.[79, 80] have studied the vibrational spectrum and its variation with temperature for an entire series of ferroelectric substances: $(NH_4)_2SO_4$, NH_4HSO_4, $RbHSO_4$, $LiH_3(SeO_3)_2$, and $NaH_3(SeO_3)_2$, at room temperature and at low temperatures near the phase transition. However, in spite of thorough experiments, they still did not find low-frequency vibrations with frequencies that declined at the Curie point. Subsequently, Zheludev, Sushchinskiĭ, et al.[51, 81] have undertaken attempts at similar studies on the classical hydrogen-bonded ferroelectric substances, Rochelle salt and triglycine sulfate, and also $NaNO_2$. Although these studies revealed a number of interesting effects involving the deformation of certain lines and even the appearance of new Raman lines, the authors had to acknowledge that they did not note low-frequency lines in the Raman spectra that changed appreciably in intensity and frequency in the phase-transi-

tion region. They advanced the hypothesis that the reason for failure seems to be that the "ferroelectric" vibration, e.g., for $NaNO_2$, is a translational type of vibration, which usually gives very weak Raman lines. It is also an essential fact that the frequency of such a vibration is too small, and may simply lie outside the experimental region.

Aref'ev, Bazhulin, et al.[50] have obtained more encouraging results in a study of similar effects in the crystals KH_2PO_4 and $NH_4H_2PO_4$. The spectra of these crystals showed a low-frequency Raman line with a maximum at 34 cm^{-1} (KH_2PO_4) or 34.5 cm^{-1} ($NH_4H_2PO_4$) at room temperature. It shifted appreciably toward the exciting line (Hg 5461 Å) as the temperature was lowered and approached the phase-transition point (θ = 123° K for KH_2PO_4, and θ = 147° K for NH_4PO_4). We note that the temperature variation of the frequency of this line is opposite to what usually happens when a crystal is cooled. These lines had the lowest frequencies at the phase-transition point, respectively 32 and 31.5 cm^{-1}. These data agree with the results of infrared studies performed by the same authors[71] and by Barker.[70] Unfortunately, these changes are quite slight. However, this agrees with the very small change in the dielectric constant of this crystal.[74] They showed in the same study that the expected considerable change in the intensity of the cited Raman line upon phase transition was not observed.

While noting the evident failures in most cases of detecting by the Raman method the effect predicted by theory that the frequency and intensity of a Raman line involving a "ferroelectric" vibration should vary, we can make the following remarks. As we stated in the theoretical part of the review (see Sec. 2), in the general case the enhancement of the intensity of the Raman line in the vicinity of the Curie point can be slight. In order to make this effect manifest, apparently we should select crystals in which the phase transition is close to critical, and the correlation between the fluctuations in neighboring volumes is weakly marked, in particular, perhaps, crystals showing a weak piezoeffect. Furthermore, if we take into account damping, which can be especially significant for a "ferroelectric" vibration, then the Raman components resulting from it on both sides of the exciting line can simply merge together, and it may prove impossible in principle to detect them. Apparently, this situation occurs in $BaTiO_3$. According to the data of infrared measurements (see Table II), the damping constant of the "ferroelectric" vibration of $BaTiO_3$ amounts to: $\gamma_3 \sim 2$–2.5. That is, in Ginzburg's formula (2.4) given above, $\nu_3 = \gamma_3 \omega_3$ exceeds the resonance frequency ω_3 by a factor of about two. Thus it is actually impossible to observe this

vibration in the Raman spectra of $BaTiO_3$.

On the other hand, it becomes an almost hopeless task for the experimenter to measure the intensity of these Raman lines, since they coincide here with the central component of the scattered light, whose intensity can itself vary at the phase-transition point.

Finally, an order-disorder phase transition is not ruled out for hydrogen-bonded ferroelectric crystals, which have been studied primarily by the Raman method. Such a transition rather resembles in nature a relaxation than a resonance transition. In such a case, the theory developed above is not at all applicable.

Here we must note another study[82] in which the problem of the dynamics of ferroelectric crystals was studied by observing the intensity of Rayleigh scattering in crystals of KH_2PO_4 and Rochelle salt. The authors relate the phenomenon of variation of the intensity of the scattered light to the anomalous behavior of the Mandel'shtam-Brillouin components. In essence, these components arise from scattering of light by the acoustic vibrations, which produce spatially periodic density inhomogeneities in the crystal. The frequency of these components of the scattering is determined by the velocity of propagation of sound in the crystal, and correspondingly, it involves the elastic parameters of the crystal structure. As we know, the latter undergo great changes in the vicinity of phase transitions. The possibility of anomalous scattering of this type from ferroelectric crystals was mentioned long ago.[83] Aref'ev, Bazhulin, et al.[82] observed an anomalous increase in the scat-
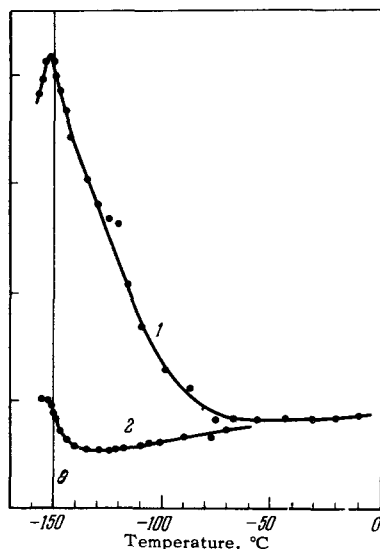

FIG. 18. Temperature-dependence of the relative intensity of scattered light in the region of the undisplaced line in an oriented single crystal of KH_2PO_4.[82] 1 — the Mandel'shtam-Brillouin scattering is determined by the anomalous elastic constant C_{66}, 2 — the Mandel'shtam-Brillouin scattering is not related to the elastic content C_{66}.
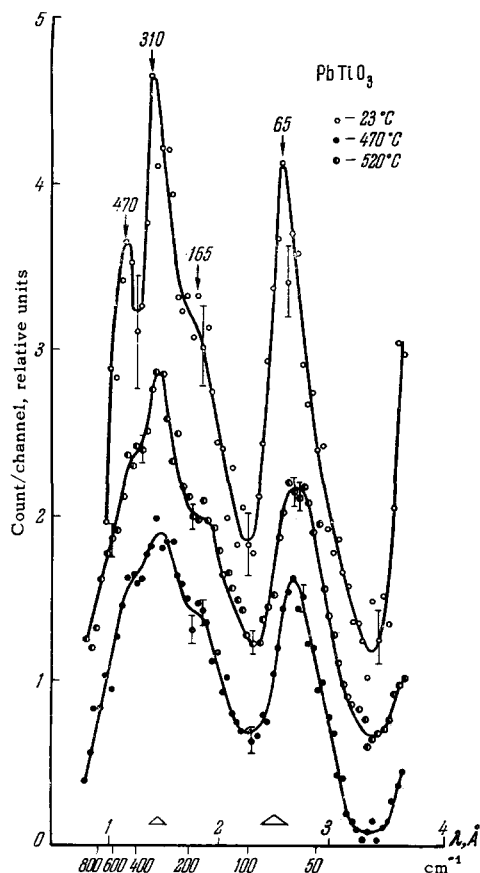
tering intensity in the region of the undisplaced frequency in the stated crystals as the temperature was lowered to the phase-transition point (Fig. 18). Upon comparing these data with other results, the authors concluded that the ferroelectric phase transition in the studied crystals is due to instability of the crystals with respect to both the optical and acoustic branches of the lattice vibration, which are related by way of the piezoeffect. This agrees with the theoretical data for ferroelectric substances showing a strong piezoeffect in the paraelectric phase (see Sec. 1, 2). An analogous effect has been observed recently in $SrTiO_3$ crystals.[122]

Since the Raman method gives direct information on the frequencies of the normal vibrations of crystals, we may hope that it will make it possible to obtain very interesting results, in spite of the great experimental difficulties.

5.3. Slow-neutron Inelastic-scattering Spectra

The first spectrum of inelastically-scattered cold neutrons by ferroelectric substances having perovskite-type structures was obtained in [84] from polycrystalline $BaTiO_3$. Spectra were obtained in [85] of cold neutrons inelastically scattered by polycrystalline $BaTiO_3$, $PbTiO_3$, and $SrTiO_3$ at room temperature. In addition, spectra were obtained for $PbTiO_3$ at 470° and 520°C, i.e., below and above the Curie point. It turned out that there were no substantial changes in the spectra of $PbTiO_3$ below and above the Curie point shown in Fig. 19, just as for $BaTiO_3$.[84] This is understandable, since changes in the spectra must involve primarily changes in the low-frequency optical branch. As we have stated, the contribution of the latter is distributed over a rather wide range of frequencies without any sharp maxima.

Figure 20 gives the results obtained in [85] and for $BaTiO_3$ and $PbTiO_3$. In the diagram, the experimental points define the scattered-neutron intensity as a function of the energy of the absorbed phonons. The solid line gives the curve obtained from the experimental data by taking the overall resolution function of the apparatus into account (using computers). Apart from some numerical discrepancies, the spectrum of $BaTiO_3$ given in Fig. 20 duplicates all the features of the analogous spectrum obtained in [84].

The low intensity of the neutrons in the spectra of $BaTiO_3$ and $PbTiO_3$ (Fig. 20) in the frequency region above 500 cm^{-1} is due to the low value of the occupation factor $\{\exp[(\epsilon/kT) - 1]\}^{-1}$, which determines the equilibrium number of phonons of energy $\epsilon \neq \hbar\omega$ at temperature T. In essence, this factor determines the limit within which experiments based on inelastic scattering of slow neutrons are possible. It makes it impossible to observe frequencies above 700–800 cm^{-1} in $BaTiO_3$-type materials. We can distinguish several peaks in the neutron spectra of $BaTiO_3$, and $SrTiO_3$

FIG. 19. Spectra of inelastically-scattered cold neutrons for
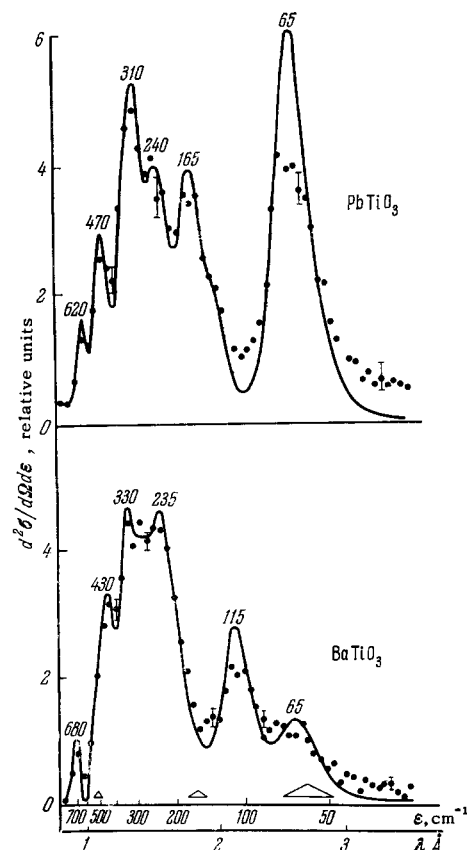PbTiO₃ at different temperatures.[85]

FIG. 20. Inelastically-scattered cold-neutron spectra for BaTiO₃
and PbTiO₃ at room temperature. The solid curves show the spectra
obtained from the experimental data with account taken of the re-
solving power of the apparatus.[85]

obtained in [85]. The part of them in the frequency
range below 100 cm⁻¹ evidently involves the acoustic
lattice vibrations. We call attention to the substantial
difference between the spectra of BaTiO₃ and PbTiO₃
given in Fig. 20, and in particular, to the absence of
a maximum in the 100-cm⁻¹ region in the spectrum
of PbTiO₃. Apparently this difference is not simply
quantitative, and perhaps we should consider it in the
light of existing indications[86] that the Ba and Pb
cations play differing roles in the origin of the ferro-
electric properties of BaTiO₃ and PbTiO₃.

Application of an analogous method based on ab-
sorption of phonons by neutrons to study hydrogen-
bonded ferroelectric substances has also shown a
lack of evident changes in the neutron spectra upon
passing from the paraelectric to the ferroelectric
state (possibly for methodological reasons, owing to
the low degree of occupation of the levels, and there-
fore, the low probability of absorbing phonons). This
applies to polycrystalline KH_2PO_4 and KD_2PO_4,[111,112]
and also to $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_2BeF_4$, and
$K_4Fe(CN)_6 \cdot 3H_2O$.[113] However, in [114] a broad band
in the region 250–450 cm⁻¹ in the infrared absorption
spectrum of KH_2PO_4 was transformed into two distinct
maxima in the vicinity of 350 and 420 cm⁻¹ upon pass-
ing through the Curie point. Since the inelastic inco-

herent neutron-scattering cross-section for hydrogen
is considerably greater than the scattering cross-
sections of the other atoms, we might expect that the
neutron spectra of the cited ferroelectric materials
should manifest various vibrations involving hydrogen
and hydrogen-containing groups like NH_4 and H_2O,
even when these vibrations are forbidden by the selec-
rules in infrared and Raman spectra.

Comparison of the neutron spectra of KH_2PO_4 and
KD_2PO_4,[111] as well as a study of the neutron and op-
tical spectra of KH_2PO_4, K_2HPO_4, and K_3PO_4,[114, 115]
has revealed a broad band in the region 600–200 cm⁻¹
in the spectrum of KH_2PO_4. It is due to the low-fre-
quency vibrations of hydrogen, and apparently is di-
rectly related to the ferroelectric transition. The en-
ergy of these vibrations is several times lower than
the energy of the ground-state (zero-point) vibrations
of the hydrogen atoms (0.079 eV according to the data
of [116]). Hence, Palevsky et al.[111] have interpreted
the cited low-frequency hydrogen vibrations as being
vibrations of hydrogen correlated with stretching vi-
brations of the oxygen atoms as in Reid's[117] model.
This gives an O—O vibration frequency of about
237 cm⁻¹, and does not presuppose an obligatory split-
ting of the vibrational ground state of the protons.

However, the results of [114] more definitely favor a splitting of the vibrational ground state of the protons into two closely-spaced levels separated by about 400 cm^{-1}. Then we can explain the low-frequency hydrogen vibrations on the basis of the idea that the hydrogen lies along the O—H⋯O bond in the paraelectric phase of KH_2PO_4 in a weakly asymmetric potential well having two minima, and it can jump quantum-mechanically from one well to the other. The dynamics of the crystal is such that the positions of the minima, whose frequencies are small in comparison with the frequency of jumping of the protons, result in a symmetrical distribution of the protons in the O—H⋯O hydrogen bond. According to this system, which agrees with the NMR data,[118] ordering must set in below the Curie point because of a considerable increase in the asymmetry of the double-minimum potential well. Consequently, the proton attaches itself to one of the oxygen atoms.

Study of the neutron spectra of $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_2BeF_4$, and $K_4Fe(CN)_6 \cdot 3H_2O$[113] showed that the ferroelectric phase transitions in these compounds do not involve large changes in the freedom of rotation of the ammonium ions and the water molecules, as NMR measurements of spin-lattice relaxation would imply.[119] Hence, to judge from the existing neutron data, the role of NH_4 ions and water molecules in the ferroelectric phase transitions of these compounds remains in doubt.

We should note that the neutron data given for KH_2PO_4, the ammonium sulfates and fluoberyllate, etc., undoubtedly require further refinement, since for various reasons the best modern methodological possibilities were not used in obtaining them. Furthermore, they came nowhere near to exhausting the potential advantages of a complex study involving not only the hydrogen-containing ferroelectric substances, but also their deuterated derivatives.

Study of single crystals of the deuterated analogs of ferroelectric substances having order-disorder phase transitions by inelastic coherent scattering of slow neutrons would make it possible to study the low-frequency "ferroelectric" branches of the vibrations without an interfering contribution from the other lattice vibrations. The latter is organically present in the inelastic incoherent scattering, both for hydrogen-containing materials and for those like $BaTiO_3$. Up to now, measurements by the inelastic coherent scattering method have been performed only on single crystals of $SrTiO_3$.

Figure 21 gives the dispersion curves for various normal vibrations of single crystals of $SrTiO_3$ measured by Cowley[14] at different temperatures in the triple-axis crystal spectrometer described in [87]. The diagram clearly shows a substantial change in the dispersion curve for the low-frequency transverse optical branch of vibrations as the temperature was
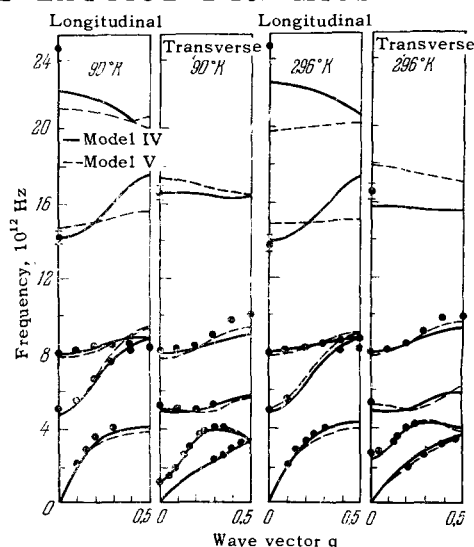

FIG. 21. Dispersion curves for $SrTiO_3$ at two temperatures.[14]

varied from room temperature to 90° K. Figure 22 shows the shape and position of the inelastic coherent neutron-scattering maxima due to the vibrations of this branch having $q \to 0$.

Figure 22 is a direct experimental proof that the frequencies of the transverse vibrations having $q \sim 0$ decrease as we approach the ferroelectric transition point. Here it turns out that the square of this frequency (Fig. 23) varies with the temperature as the reciprocal of the static dielectric constant ϵ_0, in accord with Eq. (1.22). Extrapolation to zero frequency gives a Curie point of $SrTiO_3$ near 32° K, in agreement with some known data from dielectric measurements made by a number of authors.
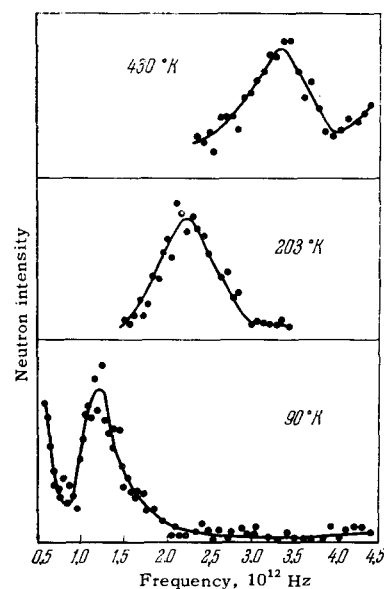
As we stated in Sec. 1.1d, Cowley has correlated

FIG. 22. Temperature-variation of the shape and position of the inelastically-scattered neutron peak for a single crystal of $SrTiO_3$.[14]
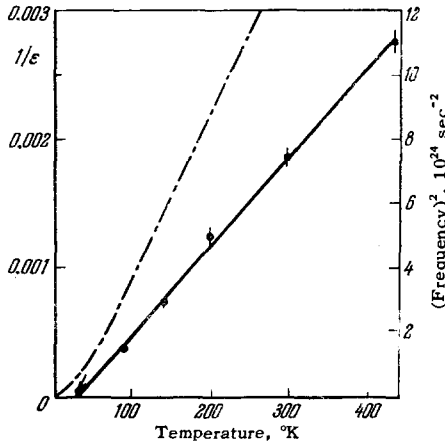
FIG. 23. Temperature-dependence of the square of the frequency (ω^2) of phonons of the low-frequency transverse optical branch of vibrations of $SrTiO_3$.[14] The dotted line gives the analogous relation for the reciprocal of the dielectric constant $(1/\epsilon)$.
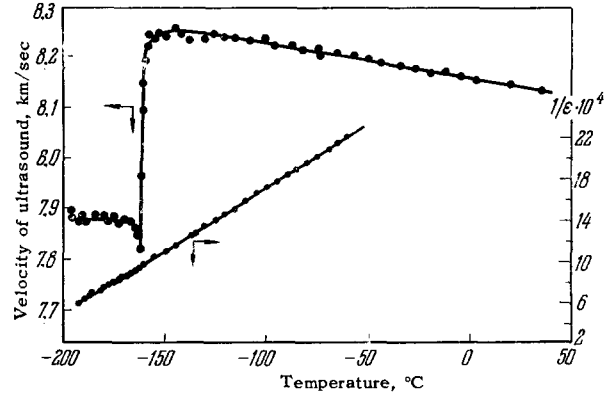

FIG. 24. Temperature-dependence of the dielectric constant ϵ and the velocity of ultrasound for a single crystal of $SrTiO_3$.[90]

the obtained results with the data from calculating dispersion curves based on six different models of the $SrTiO_3$ crystal (including the rigid-ion model and various shell models of polarizable ions having fixed or variable charges on the ions). Here the rigid-ion model involved eight adjustable parameters (the charges on the Sr and Ti ions, and six short-range force constants between the ions), while the shell models involved 14 parameters (the same eight as in the rigid-ion model, plus six parameters of electric and "mechanical" polarizability).

The values of the dielectric constant and elastic constants of $SrTiO_3$ calculated for the different models agree best with the experimental data for two models. In varying the parameters in these latter models, the effective charges of the ions proved to be close to their total charges. Figure 21 shows as solid and dotted lines the dispersion curves calculated for these two models, together with Cowley's experimental data.

Another conclusion from the results of the calculations for the various models is that one only has to make a small change in the short-range force parameters obtained to fit the room-temperature data in order to fit the experimental data at 90° K, the charges and polarizabilities of the ions remaining constant. This confirms the idea derived from the theory that a slight temperature-dependence of the interaction forces in the delicate balance of short- and long-range forces gives rise to a strong temperature-dependence of the low-frequency transverse optical vibrations.

Cowley's study of single crystals of $SrTiO_3$ by slow-neutron spectrometry has made it possible qualitatively to explain the features of the recently discovered phase transition in $SrTiO_3$ in the vicinity of 110° K.[88] According to the data of [89], the small structural distortions of $SrTiO_3$ are pseudomonoclinic in nature at liquid-nitrogen temperature (a = c = 3.887_0 kX, b = 3.898_8 kX, b/a = 1.0030, β = 90°06'); they are not accompanied by changes in the dielectric

constant at the phase-transition point, but the elastic constants vary sharply, as well as the velocity of ultrasound (see Fig. 24, taken from [90]).

We could assume with regard to the variation in the velocity of ultrasound in the phase-transition region that this transition results from instability of the cubic $SrTiO_3$ structure with respect to transverse acoustic vibrations, in analogy to the above-discussed instability of the cubic $SrTiO_3$ structure with respect to transverse acoustic vibrations, in analogy to the above-discussed instability with respect to the optical vibrations. However, Cowley[14] found no peculiarities by direct measurement of the frequency of the transverse acoustic vibrations at the phase-transition point. Hence he assumed that one can consider the phase transition in $SrTiO_3$ from the standpoint of lattice dynamics as resulting from accidental degeneracy of two branches of the frequency spectrum of $SrTiO_3$ near 90° K.

As we know (see, e.g., [15]), the isothermal elastic constants contain a term of the form

$$\frac{2n(s, q) + 1}{\omega^2_{s, q} - \omega^2_{s', q}},$$
(5.1)

where n is the number of vibrations of the type (s, q). The denominator of this term contains the difference of the squares of vibration frequencies belonging to the different branches s and s'. If now we return to the dispersion curves for $SrTiO_3$ (see Fig. 21), we can note that as the temperature is lowered from room temperature to 90° K, the low-frequency optical branch is superimposed on the longitudinal acoustic branch over a certain range of q values. In Fig. 25, this superimposition of the two different branches at 90° K is distinctly visible over a considerable range of wave numbers q.

In line with Eq. (5.1), such a fortuitous degeneracy at temperature T_a must result in a relation agreeing with the experimental data, of the type $C_{\alpha\beta\gamma\delta}$ = A + BT + C/(T − T_a). Here the last term, which depends on the frequencies and number of degenerate modes, determines the behavior of the elastic constants and

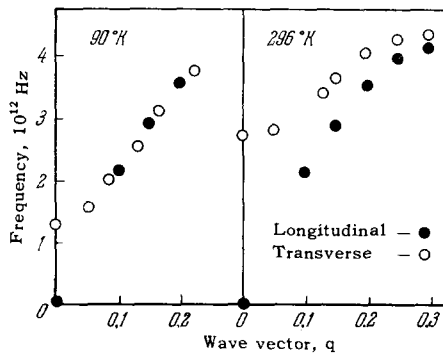FIG. 25. Positions of the acoustic and transverse optical branches of vibrations of SrTiO₃ at two temperatures.[14]

the velocity of ultrasound near T_a. Strong absorption of ultrasound occurs in the system being discussed when the frequency of the ultrasound wave is $\omega_{s,q}$ $- \omega_s', q'$.

As for the temperature-dependence of the dielectric constant, one can take simple account of the contributions to the deformation of the SrTiO₃ structure in the phase transition made by the displacements of the atoms as they take part in the longitudinal and transverse vibrations. In accord with Fig. 24, it indicates that the ϵ values for the cubic and deformed SrTiO₃ structures are equal at the phase-transition point.

5.4. On the possibility of studying the dynamics of ferroelectric substances by using the Mössbauer effect

It was shown above that as we approach the Curie point, the behavior of BaTiO₃-type materials increasingly begins to be determined by the low-frequency transverse optical branch of the lattice vibrations, the frequency of which varies according to the law $\omega = A(T - T_C)^{1/2}$. Evidently, as the role of the low-frequency optical branch is enhanced, the probability must increase that phonons belonging to this branch will participate in processes of inelastic interaction of lattice vibrations with radiation. Therefore the probability of the Mössbauer effect in resonance scattering of γ quanta should decrease anomalously as we approach the Curie point.[91, 98]

An anomalous decrease in the probability of the Mössbauer effect has been observed in BaTiO₃ for Fe[57, 92] nuclei and also Sn¹¹⁹ nuclei in Ba(Ti, Sn)O₃ solid solutions on the BaTiO₃ side.[93, 103, 106, 107] However, a negative result was obtained in [108].

Figure 26 shows the temperature-dependence of the Mössbauer effect for the solid solution Ba(Ti, Sn)O₃. To illustrate the relation of the region of the anomalous decline in the effect to the temperature of the ferroelectric phase transition, this same diagram shows the temperature-dependences of the dielectric constant and the tangent of the dielectric loss angle.

Although it is not yet clear without making a direct theoretical analysis what concrete information one can
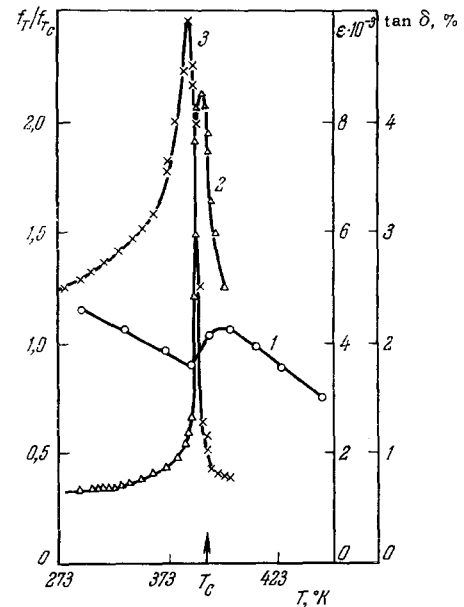

FIG. 26. Temperature-dependence of the probability f of the Mössbauer effect (curve 1), the dielectric constant ϵ (curve 2), and tan δ (curve 3) for the solid solution Ba(Ti₀.₉₉, Sn₀.₀₁)O₃.[93]

get on the parameters of the low-frequency vibrations from Mössbauer spectra of ferroelectric substances, we can expect interesting results from studies of this type.

CONCLUSION

Application of the ideas of the dynamic theory of crystals to explain ferroelectric transitions is undoubtedly an important stage in the development of our ideas on the nature of ferroelectricity.

The most substantial achievement of this theory is that it becomes possible to explain (though indeed still qualitatively) the features of the absorption spectra of different ferroelectric substances, the values and temperature-dependence of the frequencies involved in the ferroelectric lattice vibration modes. This opens up new possibilities of qualitatively determining the nature of the relations between different elements of the structure and the conditions favoring formation of ferro- and antiferroelectric configurations in different structures.

The experimental data obtained have already confirmed the fundamental assumptions of the dynamic theory of ferroelectricity, and have made it possible to discover a number of features requiring further theoretical and experimental study. However, these results are far from sufficient. In spite of well-known methodological difficulties, we need further experimental studies in order to obtain more precise and complete data on the positions and shapes of the spectral bands, and on their temperature variation, especially in the phase-transition region. Special studies are also needed to determine more exactly the forms of the normal vibrations of ferroelectric crystals, and

in particular, the form of the low-frequency vibration directly involved in the ferroelectric state.

However, we should note that it would also be unjustified at present to overestimate the possibilities of the dynamic theory as a "general theory of ferroelectric and piezoelectric crystals," and to expect the theory to agree completely with experiment for real ferroelectric substances.

In addition to the difficulties in principle, involving the necessity of taking direct and more accurate account of the influence of anharmonic effects and fluctuations, as well as a number of other factors (e.g., dissipative losses and quadrupole moments) in the fundamental dynamic equations, the procedure of direct numerical comparisons is also very complex. It is useful to recall that this required the variation of five atomic parameters even for simple alkali-halide crystals. Evidently, in a rigorous approach the number of possible variations is incomparably greater for perovskite-type crystals, not to mention more complex compounds.

In this regard, we must not consider either the possibilities of the theory or the demand for experimental data for the most varied ferroelectric materials to have been exhausted.

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