Microscopic theory of the lattice dynamics and the nature of the ferroelectric instability in crystals

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A brief review is given of model theories of the displacive structural instability in ferroelectrics. Particular attention is paid to the idea of compensation of the contributions of the short-range forces and the long-range internal field dipole forces to the square of the frequency of critical lattice vibrations. A vibronic theory of ferroelectricity is also discussed and its shortcomings are identified. A detailed analysis is made of the modern microscopic theory of lattice dynamics and exact expressions are derived for the force matrix governing the phonon spectrum of a crystal. The theory is discussed in the specific case of polar nonmetallic crystals. The example of semiconducting ferroelectrics from the group of IV–VI compounds is used to formulate rigorously the microscopic problem of the causes of the structural instability of such compounds on the basis of the exact expressions for the matrix of the force constants.

CONTENTS

1. INTRODUCTION

Ferroelectricity represents one of the most extensively studied branches of solid-state physics. Many monographs and reviews have been published on the properties of ferroelectric crystals and on the theory of ferroelectricity.[1-7] A highly advanced phenomenological theory of ferroelectricity has been developed on the basis of the ideas of Landau on second-order phase transitions involving expansion of the free energy in powers of the order parameter.

The first theory of a ferroelectric phase transition in crystals was formulated by Ginzburg[8] and was subsequently developed by many Soviet and other authors. A detailed account of the phenomenological theory of ferroelectricity can be found in several monographs,[1,5,7,9] so that in the present review we shall ignore completely the topics from this theory as well as the range of phenomena which this theory describes, confining ourselves mainly to the problems of the microscopic theory relating to the nature of ferroelectricity itself and the reasons for its appearance in crystals.

Many investigations have been made of the problem of the ferroelectric instability in crystals. The first qualitative ideas on the causes of the appearance of a spontaneously polarized state in a certain range of temperatures were put forward in the thirties by Kurchatov.[10] Later the idea of a "polarization catastrophe" as the cause of ferroelectricity of crystals was developed by Skanavi, Slater, and several other authors. However, recently theories of the structural instability in crystals have appeared and these are based on the ideas going back to the work of Fröhlich on the lattice instability in metals.[11] The use of a different nomenclature and the absence of any clear relationship between these two approaches suggests different physical mechanisms of the ferroelectric instability proposed by these theories. The problem of the nature of the ferroelectric instability in crystals is complicated also by the absence of a rigorous microscopic theory of ferroelectricity which would make it possible to go beyond the model approach and also more generally provide an opportunity for calculating the coefficients of the phenomenological expansion of the free energy, particularly for calculating the temperature of the phase transition and its dependence on the crystal and electron structures, on the nature of chemical binding, etc. The development of such a theory is an urgent task which has not yet been carried out. The purpose of the present review is to discuss models of the ferroelectric instability and feasibility of rigorous formulation of a microscopic theory of ferroelectricity on the basis of a microscopic theory of the lattice dynamics of crystals.

The anomalous behavior of the low-frequency permittivity ε_0 without any anomaly of the high-frequency (electron) permittivity ε_∞ (apart from a kink or a small discontinuity) in the vicinity of a ferroelectric phase transition is a direct indication of the important role played by the crystal lattice in the establishment of ferroelectric properties. The similarity of a phase transition in ferroelectrics to a second-order phase transition means that the crystal structure of the polarized phase can be derived by continuous distortion of the lattice of the paraelectric phase in which the characteris-

tic atomic displacements are small compared with the inter-atomic distance a_0. It is therefore natural to relate the lattice distortions in the course of a ferroelectric transition to the loss of stability by one of the normal lattice vibrations in the paraelectric phase in the range of temperatures corresponding to the polarized (ferroelectric) state. This point of view makes it possible to discuss the structural instability using the phonon language and postulating the existence of a normal vibration with an anomalous temperature dependence of its frequency near the phase transition point.

Another possibility is related to the presence of ions exhibiting a negative individual rigidity at the central (symmetric) position in the paraelectric phase.[12] This means that the potential in which such an ion moves when the other ions in the lattice occupy fixed equilibrium positions has several equivalent minima shifted from the symmetric position so that the motion of this ion would be strongly anharmonic and the phonon approach would be unsatisfactory.

The results of experimental investigations have demonstrated that there are two very distinct groups of ferroelectrics, in one of which (order-disorder materials) the situation is of the quasi-Ising type,[5,6,13] whereas in the other group (displacive ferroelectrics) the ferroelectric state appears because of the loss of stability by one of the dipole-active transverse optical lattice vibrations of the paraelectric phase at low temperatures [1,5,6]

The theoretical ideas used in microscopic descriptions of the phase transition in these two groups of ferroelectrics are very different.[5] A detailed review of the current microscopic theories of structural order-disorder phase transitions can be found in Ref. 13. The present paper will deal with the corresponding problems in the case of displacive ferroelectrics.

The general ideas on the relationship between the microscopic theory of ferroelectric phase transitions in crystals with lattice dynamics were formulated by Ginzburg,[8,14] Anderson,[15] and Cochran.[16,17]

Ginzburg developed a phenomenological theory of ferroelectricity pointing out for the first time that the coefficient in front of the quadratic term in the expansion of the free energy in powers of the order parameter, i.e., in powers of the polarization, is related directly to the elastic constant of a certain normal lattice vibration and vanishing of this constant at the second-order phase transition point should correspond to the existence in the system of a critical vibration of frequency which tends to zero when $T \to T_c$.

The subsequent formulation of the microscopic theory of the ferroelectric instability in the phonon approach and a discussion of the role of the lattice anharmonicity in stabilization of the critical vibrations at high temperatures was provided by Anderson.[15]

Cochran[16,17] used the Lyddane-Sachs-Teller relationship and its generalization to the case of polyatomic crystals, given in Ref. 17, to show that one of the dipole-active transverse optical (TO) lattice vibrations should be critical.

The ideas put forward in Refs. 8 and 14–17 have been confirmed directly by experimental investigations of the phonon spectra of various displacive ferroelectrics by the methods of infrared spectroscopy, Raman scattering of light, and inelastic scattering of thermal electrons.[1–4] which have revealed "soft" TO vibrations of the lattice in these crystals.

Formulation of a microscopic theory of phase transitions in weakly anharmonic displacive ferroelectrics in terms of the lattice (phonon) Hamiltonian was completed by Kwok and Miller[18] and by Vaks[5,19] who obtained an explicit microscopic (in the sense defined above) expression for the coefficients of a phenomenological Ginzburg-Landau expansion of the free energy in terms of the lattice Hamiltonian parameters.

However, in fact such a theory is also phenomenological because it is based on the lattice Hamiltonian the parameters of which (phonon frequencies, polarization vectors in the harmonic approximation, and tensors of the anharmonic coefficients) cannot be determined within the framework of the proposed scheme. Consequently, the most important properties of the system responsible for the existence of a ferroelectric phase transition in crystals, namely the instability of critical TO lattice vibrations at low temperatures and the temperature dependence of ω_{TO} resulting in stabilization of the TO vibrations at high temperatures,[1] are simply postulated in this theory.

This discussion of the causes of the instability of critical TO vibrations below T_c and stabilization of these vibrations above T_c belongs in fact to the microscopic theory of lattice dynamics. This determines, on the one hand, the nature of the difficulties encountered in this problem because the study of the relative stability of these or other crystal structures requires the knowledge of the total energy of the ground state (total free energy at temperatures $T > 0$ K) of a crystal considered as a function of the coordinates of nuclei.[20] On the other hand, this makes it possible to apply to displacive ferroelectrics those powerful methods which have been developed recently for lattice dynamics and which are discussed in the following sections of the present review.

The review is organized as follows: the second section deals with model theories of the structural instability in displacive ferroelectrics, the third section provides a detailed account of the modern microscopic theory of lattice dynamics and derivations of the exact expressions for the force matrix of a crystal governing its phonon spectrum. We shall discuss the corresponding theory for polar nonmetallic crystals. In the concluding section of the review we shall use the example of ferroelectric semiconductors in the form of IV–VI compounds to consider a rigorous microscopic formulation of the problem of the causes of the structural instability of these compounds on the basis of the exact microscopic expressions obtained in Sec. 3.

2. MODEL THEORIES OF THE STRUCTURAL INSTABILITY IN DISPLACIVE FERROELECTRICS

An important role in the development of a self-consistent microscopic theory of the ferroelectric instability is played by simple models, which—in contrast to formal general expressions—carry information on the qualitative features and differences between the crystal and electron structures and the nature of chemical binding of the investigated compounds.

There are two fundamentally different approaches to the problem of ferroelectric instability. The first is based on the atomic theory of ionic insulators and the method of the effective local field, utilizing the idea of compensation of the contributions of the short-range forces and the long-range internal field dipole forces to the square of the frequency of

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critical TO lattice vibrations. The second approach is developed within the framework of the band theory and is based on the electron-phonon Fröhlich Hamiltonian and on the idea of a renormalization of the spectrum of bare phonons resulting in an instability because of a strong interband electron-phonon interaction.

All known ferroelectrics are insulators or semiconductors with a higher or lower degree of ionicity, so that the simplest model accounting for the important features of ferroelectricity is that postulating point (nonoverlapping) polarizable ions with charges $Z'_s e$ and dipole electron polarizabilities of the ions α_s (s is the sublattice index).

In this model the dielectric properties of cubic crystals are described by the following system of equations[2]

$$\mathbf{P} = \sum_s \mathbf{P}_s^q, \qquad \mathbf{P}_{si}^q = -\frac{e}{v_0} Z_s^i \mathbf{U}_s^l - \frac{\alpha_s}{v_0} \mathbf{E}_{i}^q, \qquad (2.1)$$

$$\mathbf{E}_{si}^q = \mathbf{E}_i^q + \frac{4\pi}{3} \mathbf{P}_{si}^q - \sum_{t,j} \gamma_{ij}^{st} \mathbf{P}_{tj}^q - \frac{e}{v_0} \sum_{t,j} \gamma_{ij}^{st} Z_t^j \mathbf{U}_{si}^q, \qquad (2.2)$$

where $\mathbf{p}^q$ and $\mathbf{E}^q$ are the long-wavelength (macroscopic) components of the polarization and electric field intensity, $\mathbf{E}_{si}^q$ is the lattice Fourier component of the local field $\mathbf{E}_s^R$ acting on an ion $(\mathbf{R}, s)$ in a distorted lattice and described by

$$\mathbf{E}_s^q = \sum_\mathbf{R} \exp\left[-i\mathbf{q}\left(\mathbf{R} + \mathbf{R}_s\right)\right] \mathbf{E}_s^R, \qquad (2.3)$$

$\mathbf{R}$ is the lattice vector, $\mathbf{R}_s$ is the fundamental vector of the lattice structure, $\mathbf{U}_s^q$ represents long-wavelength displacements of nuclei from the equilibrium positions, $\hat{\gamma}$ is the tensor of the internal field constants representing the difference between the internal field factor and the Lorentzian factor (equal to $4\pi/3$) in a specific crystal structure, and v_0 is the volume of a unit cell.

In this model the influence of the crystal structure on the dielectric properties of a given material is described by the tensor $\hat{\gamma}$ and the influence of the electron structure is described by the dipole polarizabilities of ions α_s as well as, to some extent, by the magnitude of the ion charges if we regard the latter as effective charges differing from the ideal ion charges governed by the valence of the corresponding atoms.

The phenomenological relationship[20-22]

$$\mathbf{P}^q = -\frac{e}{v_0} \sum_s \hat{Z}(s)\, \mathbf{U}_s^q + \frac{\varepsilon_\infty - 1}{4\pi} \mathbf{E}^q, \qquad (2.4)$$

where ε_∞ is the high-frequency (electron) permittivity of a crystal and $\hat{Z}(s)$ is the tensor of the macroscopic (transverse) optical charge representing the contribution of the long-wavelength optical displacements of ions to the macroscopic polarization of a polar crystal, allows us to derive from Eqs. (2.1) and (2.2) the following expressions for the macroscopic parameters ε_∞ and $\hat{Z}$:

$$\varepsilon_\infty = 1 + \frac{4\pi}{v_0} \beta \left(1 - \frac{4\pi}{3v_0}\beta\right)^{-1}, \qquad (2.5)$$

$$\hat{Z}(s) = \left(1 - \frac{4\pi}{3v_0}\beta\right)^{-1} \hat{\zeta}(s) = \frac{1}{3}\left(\varepsilon_\infty + 2\right) \hat{\zeta}(s), \qquad (2.6)$$

$$\hat{\zeta}(s) = \sum_t \left[\left(\hat{I} - \frac{1}{v_0}\hat{\alpha}\hat{\gamma}\right)^{-1}\right]^{ts} \sum_u \left(\hat{I} - \frac{1}{v_0}\hat{\alpha}\hat{\gamma}\right)^{su} Z_u^i, \qquad (2.7)$$

$$\beta\delta_{ij} = \sum_{s,t}\left[\left(\hat{I} - \frac{1}{v_0}\hat{\alpha}\hat{\gamma}\right)^{-1}\hat{\alpha}\right]_{ij}^{st}, \qquad (\hat{\alpha})_{ij}^{st} \equiv \delta_{st}\delta_{ij}\alpha_s; \qquad (2.8)$$

here, $\hat{I}$ is a unit tensor. The relationship (2.5) is similar to the familiar Lorenz-Lorentz formula for ε_∞, but generally speaking even in the case of cubic crystals the value of β in this formula is not equal to the sum of the polarizabilities of ions in a unit cell. It should be noted that the condition of electrical neutrality of a unit cell in a crystal $\sum_s Z'_s = 0$ yields automatically, when Eqs. (2.6) and (2.7) are used, the sum rule for $\hat{Z}(s)$:

$$\sum_s Z_{ij}(s) - \frac{1}{3}\left(\varepsilon_\infty + 2\right)\left(\sum_s Z_s^i\right)\delta_{ij} = 0. \qquad (2.9)$$

The low-frequency dielectric properties of a crystal can be described if we supplement Eqs. (2.1) and (2.2) with the equation of motion for the ions (nuclei), which in the model under discussion is[20]

$$M_s\omega^2 \mathbf{U}_i^q = \sum_{t,j} R_{si,\,tj}(\mathbf{q})\, \mathbf{U}_{tj}^q - Z_s^i e \mathbf{E}_{si}^q + \sum_{t,j} \left[Z_t^i e\,(\hat{\gamma}\hat{\alpha})_{ij}^{ts}\right]\mathbf{E}_{sj}^q, \qquad (2.10)$$

where $\hat{R}$ is the contribution of the short-range forces to the force matrix, whereas the second and third terms on the left-hand side of the above equation describe (in the dipole approximation) the long-range Coulomb forces acting on an ion in a distorted lattice (in an approximation which is linear in $\mathbf{U}_s^q$). The second term is determined by the force acting on the ion charge and the third by the force acting on the induced electron dipole moment of the ion.[20]

Solving the system of equations (2.1), (2.2), and (2.10) and allowing for the relationships (2.4)–(2.8), we readily obtain the following expressions for the dynamic (dispersion) equation describing the spectrum and polarization vectors of long-wavelength optical phonons in the harmonic approximation, for the force matrix $\hat{\Phi}(\mathbf{q}\to 0)$, and for the low-frequency permittivity[3] ε_0:

$$\omega^2 e_{si} = D_{si,\,tj}(\mathbf{q})\, e_{tj}, \qquad \hat{D}_{st} = \frac{\hat{\Phi}_{st}}{(M_s M_t)^{1/2}}, \qquad (2.11)$$

$$\hat{\Phi}_{st}(\mathbf{q}\to 0) = \hat{\Phi}_{st}(0) + \hat{Z}^+(s)\cdot\frac{4\pi e^2}{v_0}\,\hat{\mathscr{P}}^L\hat{Z}(t), \qquad (2.12)$$

$$\mathscr{P}_{ij}^L \equiv n_i n_j, \qquad n_i = \frac{q_i}{q}, \qquad$$

$$\hat{\Phi}_{st}(0) = \hat{R}_{st}(0) + \hat{C}_{st}(0), \qquad (2.13)$$

$$\hat{C}_{st}(0) = -\frac{4\pi e^2}{v_0}\hat{Z}^+(s)\frac{\hat{I}}{\varepsilon_\infty + 2}\hat{Z}(t) + \tilde{C}_{st}(0); \qquad (2.14)$$

$$\tilde{C}_{st}(0) = \frac{e^2}{v_0}\sum_u Z_u^i \left(\hat{I} - \frac{1}{v_0}\hat{\gamma}\hat{\alpha}\right)^{us}\left[\left(\hat{I} - \frac{1}{v_0}\hat{\gamma}\hat{\alpha}\right)^{-1}\hat{\gamma}\right]^{st}Z_t^i$$

$$- \frac{e^2}{v_0}\sum_u Z_u^i\left(\hat{I} - \frac{1}{v_0}\hat{\gamma}\hat{\alpha}\right)^{us}\left[\left(\hat{I} - \frac{1}{v_0}\hat{\gamma}\hat{\alpha}\right)^{-1}\right]^{st}\sum_v \hat{\gamma}^{tv}Z_v^i,$$

$$\varepsilon(\omega)\delta_{ij} = \varepsilon_\infty\delta_{ij} + \frac{4\pi e^2}{v_0}\sum_{s,t}\left\{\frac{\hat{Z}(s)}{M_s^{1/2}}\left[(\hat{D} - \omega^2\hat{I})^{-1}\right]^{st}\frac{\hat{Z}^+(t)}{M_t^{1/2}}\right\}_{ij}, \qquad (2.15)$$

$$\varepsilon_0\delta_{ij} = \varepsilon_\infty\delta_{ij} + \frac{4\pi e^2}{v_0}\sum_{s,t}\left\{\hat{Z}(s)\left[\hat{\Phi}(0)^{-1}\right]^{st}\hat{Z}^+(t)\right\}_{ij}. \qquad (2.16)$$

The expressions (2.5)–(2.8) and (2.11)–(2.16) are equivalent to the corresponding relationships of Born and Huang (Chap. 5 in Ref. 20) and are given here in a form convenient in subsequent discussions.

Because of the condition (2.9) the Coulomb contribution to the force matrix satisfies automatically the sum rule

$$\sum_s \Phi_{si,\,tj}(\mathbf{q}\to 0) = \sum_t \Phi_{si,\,tj} \quad (\mathbf{q}\to 0) = 0, \qquad (2.17)$$

which is a consequence of the invariance of the total energy of the system in the presence of an adiabatically slow displacement of all the nuclei in a crystal as a whole[20] and ensures the existence of acoustic vibrations of the lattice in insulators.

We shall now discuss some features of the derived expressions. First of all, we note that the total Coulomb contribution to the force matrix consists of two parts: a regular one in the limit $\mathbf{q}\to 0$ described by the matrix $\hat{C}$ in Eq. (2.14) and a part which is nonanalytic in the limit $\mathbf{q}\to 0$ described by the second term in Eq. (2.12). The nonanalytic part is related to a macroscopic field which appears in the case of longitudinal dipole-active optical vibrations of the lattice and is responsible for the splitting between the LO and TO frequencies in polar crystals. The frequencies of dipole-active TO vibrations are governed by the regular part of the force matrix of Eq. (2.12). It is usual[5] to assume that ω_{TO}^2 can be described by

$$\omega_{TO}^2 = \omega_0^2 - \omega_{DD}^2, \qquad (2.18)$$

where ω_0^2 is the positive contribution of the short-range forces (i.e., the contribution of $\hat{R}$), whereas ω_{DD}^2 is the negative contribution of the regular part of the dipole-dipole internal field interaction, i.e., the contribution of $\hat{C}$. It should be noted that if an allowance is made for the matrix $\hat{\gamma}$, a rigorous proof of the general conclusion about the signs of these quantities cannot be provided, although in many situations Eq. (2.18) is satisfied and in the case of normal insulators the value of ω_0^2 is several times higher than ω_{DD}^2, which ensures stability of the TO lattice vibrations in these crystals. From the point of view of Eq. (2.18) the instability of one of the TO lattice vibrations occurs when

$$\omega_0^2 < \omega_{DD}^2 \qquad (2.19)$$

and is possible either because of the anomalous reduction in ω_0^2 or because of an anomalous increase in ω_{DD}^2. A clear choice between these two alternatives is difficult for a number of reasons. The first reason is the limited validity of the very model of polarizable point ions in the description of crystals which have ferroelectric properties, because usually such crystals have a lower ionicity than normal ionic crystals and are more likely to be semiconductors than insulators. For example, in the case of alkali halide crystals the band gap is $E_g \sim 7$–10 eV, whereas in ferroelectrics with the perovskite structure the band gap is $E_g \sim 1$–4 eV and in ferroelectrics which are IV–VI compounds and have the NaCl structure in the paraelectric phase the corresponding value is $E_g \sim 0.2$–0.3 eV.

The second reason is the considerable indeterminacy in the choice of the parameters of the model such as the polarizabilities and charges of ions and of the parameters representing the short-range forces. Calculations carried out for several compounds with the NaCl and CsCl structures, for which the model parameters can be determined directly from the experimental values of ε_∞, ω_{TO}, and ω_{LO} (Ref. 20), demonstrate that the polarizabilities and charges of ions differ from the corresponding values for free ions. In the case of alkali halide crystals these differences are small. For example, if the valence is unity, the ion charge Z^i which occurs in

Eqs. (2.6), (2.7), and (2.12)–(2.16) is of the order of 0.8–0.9 (Ref. 20). Hence, Tolpygo[23] could use the tight-binding approximation to develop a microscopic theory of dipole forces in alkali halide crystals with the NaCl-type crystal structure selecting as the zeroth order approximation the hypothesis of nonoverlapping ions and allowing for the distortion of the wave functions of the ions because of their overlap on the basis of perturbation theory. However, such a theory can hardly be applied to IV–VI compounds, in which the effective ion charge Z^i is almost four times less than the valence of two.

Leaving aside the problems of validity of the model of polarizable ions in the description of lattice dynamics and dielectric properties of displacive ferroelectrics (we shall return to this topic later), we shall discuss the qualitative conclusions which can be drawn from an analysis of the causes of the instability of the TO lattice vibrations in cubic ionic crystals on the basis of this model.

We shall begin with the simplest case of diatomic cubic crystals in which the internal field is Lorentzian,[20] i.e., it is necessary to substitute $\hat{\gamma}=0$ in Eqs. (2.5)–(2.10) and (2.14). We then obtain the following expressions for the frequencies of the optical lattice vibrations[20]

$$\omega_{TO}^2 = \omega_0^2 - \omega_{DD}^2, \qquad (2.20)$$

$$\omega_{LO}^2 = \omega_{TO}^2 + \frac{Z^2}{\varepsilon_\infty}\Omega^2, \qquad \Omega^2 \equiv \frac{4\pi e^2}{\mu v_0}, \qquad (2.21)$$

μ is the reduced mass of a unit cell, and

$$\omega_{DD}^2 = (\varepsilon_\infty + 2)\left(\frac{Z^i}{3}\right)^2\Omega^2 - \frac{Z^2}{\varepsilon_\infty + 2}\Omega^2. \qquad (2.22)$$

In Eq. (2.22) an allowance is made for the fact that the scalar macroscopic charge Z is related to the effective ion charge Z^i by [Eqs. (2.6) and (2.7)]

$$Z = \frac{1}{3}(\varepsilon_\infty + 2)Z^i, \qquad Z = |Z_s|, \qquad Z^i = |Z_s^i|. \qquad (2.23)$$

It follows from Eqs. (2.20), (2.22), and (2.23) that an increase in the contribution of the dipole forces to ω_{TO}^2, i.e., instability of TO lattice vibrations, is favored by an increase in the electron permittivity ε_∞; at the same time there should be an increase in the macroscopic charge Z. This is precisely the tendency observed for compounds with the NaCl and CsCl structures. This tendency is manifested most strongly in the case of IV–VI compounds. The problem of the influence of dipole forces on the stability of TO lattice vibrations in diatomic cubic crystals will be discussed in greater detail in Sec. 4.

We shall now consider polyatomic cubic ferroelectrics with the perovskite structure. Calculations of the internal fields in crystals with this structure[24-26] have shown that such fields are not Lorentzian and that the individual structure constants of the internal field γ_{ij}^{st} reach values of the order of 30, i.e., they are almost an order of magnitude larger than the Lorentzian factor $4\pi/3$. Bearing in mind that the electron polarizability of these compounds is not very large ($\varepsilon_\infty \sim 5$–$7$—see Ref. 27), we can expect the presence of anomalously large structure constants of the internal field to play an important role in the ferroelectric instability of these compounds, giving rise to an anomalously large contribution of the dipole forces to one of the frequencies of TO vibrations of the lattice in the cubic phase. These ideas were first

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put forward by Skanavi[26,28] and Slater.[29] They used the single-ion model in the first approximate calculations relating to barium titanate ($BaTiO_3$) which confirmed this hypothesis. It was found that the difference between the internal and the Lorentzian fields has little effect on the value of ε_∞ because of the approximate equality of the electron polarizabilities of barium and oxygen, but has a strong influence on the low-frequency permittivity ε_0. The calculation carried out by Slater demonstrated that in the single-ion approximation (assuming that the titanium ions are ferroelectrically active) a simultaneous allowance for the electron polarizabilities of barium and oxygen ions and for the difference between the internal and Lorentzian fields increases the dipole contribution to the frequency of the critical TO vibration by a factor of about 16, whereas an allowance for the difference between the internal and Lorentzian fields (ignoring electron polarizabilities of the ions) increases this frequency approximately by a factor of 6, compared with the approximation in which the internal field is regarded as Lorentzian and the ions are regarded as hard.

However, calculations carried out by Skanavi and Slater cannot be regarded as fully satisfactory because they used the single-ion approximation and also because of inaccurate calculations of the local effective (polarizing) field [no allowance was made for the last term in Eq. (2.2)][30] and of the Coulomb contribution to the force acting on an ion in a distorted lattice [the force acting on an induced electron dipole moment of the ion, represented by the last term in Eq. (2.10), was ignored]. A self-consistent calculation of the frequencies of optical lattice vibrations of the cubic phase of $BaTiO_3$ by means of Eqs. (2.11)–(2.14) was made by Dvořak and Janovec.[31,32] A group-theoretic analysis of long-wavelength lattice vibrations in the perovskite structure[33] was made by these authors[31,32] and they found the frequencies of all four optical branches of the lattice vibration spectrum of barium titanate (without allowance for the splitting caused by the macroscopic field). Three of these branches were dipole-active. The frequency of one of the dipole-active TO lattice vibrations was found to lie well below the remaining three frequencies and was sensitive to the selection of the parameters representing the Coulomb contribution to the dynamic matrix. The calculations reported by Dvorak and Janovec were carried out varying the electron polarizabilities of the ion α_s and the effective ion charges Z_s^i. The magnitude of ion charges was varied by altering the scaling factor r, common to all the ions

$$Z_s^i = r Z_s^v,$$

where Z_s^v represents the ideal ion charges corresponding to the ion valences ($Z_{Ba}^v = 2$, $Z_{Ti}^v = 4$, $Z_O^v = -2$). It was found that if α_s was selected to be one of the values obtained by Slater from the optical data, then one of the dipole-active TO frequencies vanishes at $r = 0.226$, in good agreement with the conclusion of Slater that the effective charge of titanium is more likely to be 1 than 4 (Ref. 29). On the other hand, when the electron polarizabilities of the ions are ignored completely, i.e. in the model of rigid ions, the instability occurs only for $\gamma = 1.7$ (Ref. 32). The frequencies of the remaining three optical branches are of the usual order of magnitude and they vary slightly when the parameters of the long-range interactions are altered. The treatment given in Ref. 32 dealt also with the influence of changes in the lattice

constant on the optical frequencies. It was found that a change in the lattice constant has a strong influence on the frequency of critical TO vibrations, but has little effect on the remaining frequencies. Then, in the model of rigid ions the critical frequency decreases on increase in the volume of a crystal, in agreement with the experimental observation that the compression of a crystal stabilizes the cubic phase and lowers T_c (Ref. 5). However, in the model of polarizable ions the frequency of the critical vibrations increases on increase in the volume.[32] The discrepancy from the experimental dependence may be due to neglect of the volume dependence of the ion polarizabilities α_s. In fact, it follows from the Lorenz-Lorentz formula that the absence of the volume dependence of α_s always reduces ε_∞ on increase in the volume (because of an increase in v_0) and, consequently, it reduces the dipole contribution to ω_{TO}^2, i.e., it increases ω_{TO}^2.

Unfortunately, Dvořak and Janovec[31,32] ignored the case of the Lorentzian internal field when $\hat{\gamma} = 0$. Therefore, the influence of anomalously large structure constants of the internal field in perovskites on the stability of critical TO vibrations can be judged only on the basis of the approximate calculations of Slater and Skanavi.

It follows that the results of an analysis of the diatomic cubic crystals and compounds with the perovskite structure demonstrate that the dipole-dipole interaction is a possible cause of the ferroelectric instability in displacive materials.

An analysis of the dipole Coulomb forces as a possible reason for the lattice instability in the displacive ferroelectrics is in our opinion a natural approach because all the known ferroelectrics are ionic crystals and ferroelectric properties are a consequence of instability of the dipole-dipole transverse optical lattice vibrations without any tendency for the dipole inactive optical frequencies to decrease in perovskites which would be expected if the smallness of ω_0^2, i.e., the weakness of the short-range forces, had been significant. Moreover, there is no significant difference between the elastic constants of ferroelectrics and of normal (nonferroelectric) insulators, which is to be expected if the dominant role is played by the dipole forces, because inclusion of the electron polarizabilities of ions has a significant influence on the values of ω_{DD}^2 and ω_{TO}^2 but does not affect their elastic constants, at least in the case of centrosymmetric crystals. Use of the model of point polarizable ions for the description of the dipole forces also seems to be justified at least qualitatively, because the model of such ions contains only those parameters which have a direct physical meaning and the smallest number of such parameters is used. Moreover, the model of point polarizable ions is the simplest nontrivial exactly soluble model allowing for the direct Coulomb interaction both of the electron-ion and of the electron-electron type, which is important because (as stressed in the Introduction) the lattice stability is governed by the total energy of a crystal when the interaction is allowed for. Finally, it is equally important that the model in question yields correct order-of-magnitude estimates of a number of quantities describing the phase transition in displacive ferroelectrics.[5,8,29]

On the other hand, in addition to arguments in support of the model of polarizable point ions it is possible to provide seemingly convincing arguments based on physical considerations and demonstrating that this model cannot be used

directly to describe the contribution of electrons to the dipole-dipole interaction in semiconductors, i.e., in compounds with strongly delocalized valence electrons.[21,34,35] The situation in narrow-gap IV–VI semiconductor compounds is particularly difficult because the model of polarizable point ions is known to be unsuitable for the description of these materials. Attempts to refine the model allowing for the characteristic features of IV–VI compounds[21,34,35] have led to the conclusion that there is no relationship between the large values of ε_∞ of IV–VI compounds and their ferroelectric properties. The same conclusion, although based on more formal considerations, was reached in Ref. 36.

It therefore follows that the problem of the role of dipole forces in the case of a phase transition in a displacive ferroelectric must be solved going beyond the framework of the model of the dipole-dipole interaction in nonmetallic crystals.

We shall now consider the energy band approach to the problem of the lattice instability of displacive ferroelectrics. Different variants of the band approach[37–40] begin with the concept of noninteracting bare critical TO phonons and valence electrons. Such bare TO phonons describe stable lattice vibrations. If we include the electron-phonon interaction of the Fröhlich type, i.e., if we go to the first order in respect of the ion displacements, the frequencies of the critical TO vibrations become renormalized. In the harmonic approximation, corresponding to the second order of perturbation theory in respect of the electron-phonon interaction, the contribution of the valence electrons to ω_{TO}^2 is automatically negative because inclusion of any interaction in the second order of perturbation theory always lowers the ground-state energy.[41] Consequently, the renormalized vibration frequency becomes smaller than the bare frequency. If the electron-phonon interaction is sufficiently strong, this correction may exceed the square of the bare frequency and an instability appears. Since such reasoning applies completely to the case of any other normal lattice vibrations and any electron-phonon interaction of the Fröhlich type, it follows that even within this framework we face a number of questions such as: Why is it that the dipole-active TO vibrations become unstable? Why do these vibrations remain stable in normal (nonferroelectric) insulators and semiconductors? What are bare phonons? There are also other questions.

We also face a series of problems relating to the validity of the approach based on the Fröhlich Hamiltonian in describing the lattice dynamics of nonmetallic crystals. It is known that this approach is invalid in the case of metals.[42,43] The shortcomings of the approach in the description of lattice dynamics remain in the case of nonmetallic crystals and this applies in particular to the influence of the Coulomb electron-electron interaction on the renormalization of the phonon frequencies and the associated question of the screening of the electron-phonon interaction. Moreover, in discussing optical vibrations in nonmetallic crystals we have to deal with the role of the non-Fröhlich terms (i.e., of terms of the second order in respect of the ion displacements) in the electron-phonon interaction, which renormalize the phonon frequencies in the first order of perturbation theory and generally stabilize TO vibrations. However, we shall postpone a discussion of these problems and return to them after reviewing the current status of the microscopic theory of lattice dynamics.

3. MICROSCOPIC THEORY OF LATTICE DYNAMICS

3.1. Calculation of the electron contribution to the dynamic matrix

The microscopic approach to the calculation of the electron contribution to lattice dynamics is based on the very old idea of Born and Oppenheimer[44] on the adiabatic separation of the slow motion of nuclei and the fast motion of electrons when the energy of molecules is calculated. A similar calculation was later generalized to crystals. The essence of this approximation is as follows. If we allow for the considerable difference between the velocities of electrons and ions related to $(m/M)^{1/2}$, where m is the mass of an electron and M is the mass of a nucleus, we obtain two uncoupled (apart from small nonadiabatic corrections) systems of electrons and nuclei. The former is described by the Schrödinger equation for electrons in a field with an arbitrary distribution of nuclei

$$(T_e + V_{ee} + V_{ne}) \, \psi_v \, (r, \, R) \, = E_v \, (r, \, R) \, \psi_v \, (r, \, R), \quad (3.1)$$

where T_{ee} is the kinetic energy of electrons, V_{ee} is the Coulomb electron-electron interaction, and V_{ne} is the nuclear-electron interaction. The nuclear system is described by the following equation:

$$(T_n + V_{nn} + E_v \, (R)) \, \chi \, (R) \, = E\chi \, (R), \quad (3.2)$$

where T_n is the kinetic energy of the nuclei, V_{nn} is the Coulomb interaction of the nuclei, and $E_v(R)$ is the energy of electrons which is obtained from Eq. (3.1) and which occurs in the equation for the nuclei as a potential energy additional to V_{nn}.

Because of lack of space we shall not deal in detail with studies of the limits of validity of the adiabatic approximation: this subject is discussed in detail in, for example, the reviews of Brovman and Kagan[42] and Maksimov[43] and instead we shall give a brief summary of the current ideas.

a) In the calculation of the phonon spectra of crystals in the harmonic approximation we can ignore the nonadiabatic corrections for crystals of any type (insulators, semiconductors, and metals). In the case of nonmetallic crystals the nonadiabatic corrections to the frequencies of the majority of normal lattice vibrations are small in respect of the parameter $\bar{\omega}/E_{av}$, where $\bar{\omega}$ is the characteristic phonon frequency and E_{av} is the average width of the band gap which is of the order of several electron volts or more. In metals, there is no gap in the spectrum of electron excitations, the smallness of the nonadiabatic corrections to the phonon frequencies is governed—as shown by Brovman and Kagan[45] and Chester[46]—by the parameter ω/ε_F, where ε_F is the Fermi energy of electrons. This is due to the fact that the formation of the phonon spectrum of metals is influenced by all the electrons under the Fermi surface and the nonadiabaticity is important only in the case of electrons in a thin layer of thickness $\bar{\omega}$ near the Fermi surface.

This applies to the phonon spectrum of a crystal as a whole. In the case of individual small groups of phonon frequencies, we find that in semiconductors there may be situations in which the nonadiabaticity effects become important. For example, in the case of pure zero-gap semiconductors inclusion of the nonadiabaticity results in significant renormalization of the velocity of sound in the case of excitations

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with a sufficiently long wavelength.[4'] A different case is encountered in polar semiconductors in the presence of free carriers and it is related to the strong interaction of longitudinal optical lattice vibrations with longitudinal excitations of the carrier charge density (plasmons).[48] However, it should be pointed out that in these and in other possible cases we are speaking of the influence of the nonadiabaticity on the frequencies in the spectrum of lattice excitations determined in the harmonic approximation from the dynamic equation

$$\omega^2 e_\sigma = D_{\sigma\sigma'}(\mathbf{q}, \omega) e_{\sigma'}, \tag{3.3}$$

where $\hat{D}(\mathbf{q}, \omega)$ is the dynamic matrix and e_σ are the polarization vectors. The frequency dependence of the dynamic matrix is governed by the frequency dependence of the electron contribution, which can be expressed in terms of the total longitudinal susceptiblity of the electron subsystem $\hat{\chi}(\omega)$ (this is discussed later) and is due to the delay of the electron response to the change in the potential of the nuclei δV_{ne} caused by their displacements from equilibrium positions, in other words, it is due to the nonadiabaticity of the electron motion. Therefore, the adiabatic approximation corresponds to the use of the static value of $\hat{\chi}(\omega)$ in calculations of the electron contribution to $\hat{D}$. If we allow for the anharmonic effects, we find that the interaction-renormalized phonon spectrum is described by an equation analogous to Eq. (3.3), in which $\hat{D}$ is replaced with the quantity[5]

$$\hat{\Gamma}(\mathbf{q}, \omega) = \hat{D}(\mathbf{q}, \omega) + \hat{\Sigma}(\mathbf{q}, \omega), \tag{3.4}$$

where $\hat{\varepsilon}(\mathbf{q}, \omega)$ is the self-energy part describing the effects of the phonon-phonon interaction.

The following circumstance will be important in our later discussions. The coefficients of the terms quadratic in displacements of the nuclei, which occur in the expansion for the free energy and which govern the stability of a crystal against the displacements, can be expressed directly in terms of the static values of $\hat{\Gamma}(\mathbf{q}, 0)$ (Ref. 5). Therefore, in the harmonic approximation the problem of stability of the crystal lattice can be reduced directly to calculation of the phonon spectrum of a crystal in the adiabatic approximation and the problem of the nonadiabatic corrections to the phonon frequencies is important only when we discuss the spectrum of excitations of a system ignoring the problem of the lattice stability.

Therefore, the term "vibronic theory of ferroelectricity" used by several authors (see, for example, Ref. 40 and the literature cited there) stressing the important role of the vibronic effects, i.e., of the effects associated with the nonadiabaticity of the electron subsystem, is a totally unjustified attempt to apply to the theory of crystals the terminology taken from the theory of molecules. Moreover, in all the investigations where this terminology is employed every calculation is carried out in fact in the adiabatic approximation in the sense defined above in connection with the dynamic equation (3.3).

b) In the case of the electron subsystem the effects associated with nonadiabaticity are often a decisive influence. This applies to transport phenomena in metals and semiconductors, to the polaron effect in insulators, to the temperature dependence of the band gap of narrow-gap semiconductors, etc.

It is clear from the above discussion that the first stage of any microscopic calculation of lattice dynamics involves evaluation of the energy of the ground state of the electron subsystem as a function of the coordinates of the nuclei, which are the sources of the external field acting on electrons. The problem is solved most readily in the case of normal metals, when it is possible to carry out self-consistently the procedure of expansion (as a perturbation series) in terms of a weak electron-ion pseudopotential (for a review see Ref. 42). The situation is much more complex in the case of transition metals and also in the case of semiconductors and insulators. However, considerable progress has been made in solving this problem. The framework of a self-consistent standard many-body theory has been used to derive formally the exact expression for the total electron contribution of the harmonic and anharmonic force constants of the lattice in terms of the corresponding linear and nonlinear susceptibilities of the electron subsystem (see Refs. 43 and 49–54). We shall return to this approach later, but at present we want to consider the existing methods for calculating the total energy of a crystal.

In the case of crystals consisting of saturated "elementary" units (ions, atoms, or molecules with filled electron shells) the cohesive energy can be calculated also by perturbation theory methods. After separation of the Coulomb (Madelung) cohesive energy of ionic compounds, the remainder is due to short-range forces and is related mainly to overlap of neighboring ions. In the first approximation, the energy is equal to the average value of the Hamiltonian calculated using unperturbed wave functions of the free ions. The distortion of these wave functions leads to corrections of higher order in perturbation theory. The first calculations of this type were made by Landshoff[55] and Löwdin[56] for alkali halide crystals. However, in some cases the distortion of the wave functions must be taken into account right from the beginning. This is true also of crystals with the van der Waals interaction, which appears in the second order of perturbation theory when dealing with the optical vibrations of the lattice, etc.

The most general and rigorous method for the calculation of the ground-state energy of a system of interacting electrons in an external static local potential is at present the density functional method proposed by Kohn, Hohenberg, and Sham[57,58] (see also the reviews in Refs. 59 and 60 and the collective monograph of Ref. 61), which we shall now briefly describe.

The method is based on the following theorem proved by Hohenberg and Kohn:

1) The energy of the ground state of a system of identical zero-spin fermions with an arbitrary interaction, which experience a scalar local static potential, is a single-valued functional of the particle number density

$$E = E\{n(\mathbf{r})\}. \tag{3.5}$$

2) For a fixed number of particles, i.e., if

$$\int d\mathbf{r}\, n(\mathbf{r}) = N,$$

this functional reaches its minimum value in relation to variation of the density $n(\mathbf{r})$ when the density is equal to the exact value for the ground state of the system, i.e., when

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$$\frac{\delta E\{n\}}{\delta n}\Big|_{n=n_0(\mathbf{r})}=0. \qquad (3.6)$$

Subsequently the Kohn-Hohenberg theorem has been generalized to the case of particles with spin, to the relativistic situation, to finite temperatures, etc.[60] The energy functional $E\{n\}$ can be written in the form[62]

$$E\{n\}=T\{n\}+\int d\mathbf{r}\,n(\mathbf{r})\,V_{\mathrm{ext}}(\mathbf{r})$$
$$+\frac{e^2}{2}\int d\mathbf{r}\,d\mathbf{r}'\,\frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\widetilde{E}_{\mathrm{xc}}\{n\}. \qquad (3.7)$$

Here, $T\{n\}$ is the kinetic energy functional and the second term is the energy of the interaction with an external field which in the case of crystals can be written in the form

$$V_{\mathrm{ext}}(\mathbf{r})=\sum_{\mathbf{R}}V_{\mathrm{ne}}(\mathbf{r}-\mathbf{R}),$$

where V_{ne} is the nuclear-electron potential and $\mathbf{R}$ represents equilibrium coordinates of the nuclei. The third term in Eq. (3.7) is the contribution of the direct Coulomb electron-electron interaction (Hartree energy), whereas the last (fourth) term represents an exchange-correlation functional describing the contribution of the exchange-correlation electron-electron interaction to the potential energy of the system.

Unfortunately, more or less exact expressions for the functionals of the kinetic and exchange-correlation energies, needed for specific calculations, are available only for a homogeneous electron gas. In the case of a noninteracting electron gas the kinetic energy functional is of the form

$$T\{n\}=C_0\int d\mathbf{r}\,n^{5/3}(\mathbf{r}). \qquad (3.8)$$

The functional of the exchange-correlation energy considered in the homogeneous case can be written in the form

$$\widetilde{E}_{\mathrm{xc}}\{n\}=\int d\mathbf{r}\,\varepsilon_{\mathrm{xc}}(n(\mathbf{r})), \qquad (3.9)$$

where $\varepsilon_{\mathrm{xc}}(n)$ is the function of the density known from Monte Carlo calculations for a wide range of densities.[63] In the simplest case when only the exchange effects are taken into account, we have

$$\varepsilon_{\mathrm{xc}}(n)=C_2 n^{4/3}; \qquad (3.10)$$

here, C_0 and C_2 are constants independent of the density. The use of Eqs. (3.8)–(3.10) leads directly to a functional in the Thomas-Fermi-Dirac theory known already in the thirties:

$$E_{\mathrm{TFD}}\{n\}=C_0\int d\mathbf{r}\,n^{5/3}(\mathbf{r})+\int d\mathbf{r}\,n(\mathbf{r})\,V_{\mathrm{ext}}(\mathbf{r})$$
$$+\frac{e^2}{2}\int d\mathbf{r}\,d\mathbf{r}'\,\frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+C_2\int d\mathbf{r}\,n^{4/3}(\mathbf{r}). \quad (3.11)$$

We shall not describe this theory and its applications (the reader is referred to Refs. 60, 61, and 64 for details), but discuss briefly only some calculations of the ground-state energy and of some other static properties carried out by this method in the case of several ionic and molecular crystals. The main idea of these calculations is, as in the Löwdin method,[56] that in the first approximation these crystals can be regarded as consisting of elementary units (ions, atoms,

and molecules) with closed electron shells. This makes it possible to carry out accurate calculations of the electron density of a crystal using the wave functions of free ions, atoms, or molecules found—for example—by the Hartree-Fock method and considering the total electron density as a superposition of the densities of the individual elementary units. Substituting the density $n(\mathbf{r})$ found in this way into the functional of Eq. (3.11), we can determine the ground-state energy of the investigated system and by minimizing it with respect to the lattice parameters, we can deduce the equilibrium values of these parameters. In this approximation the cohesive energy is given by the expression

$$\Delta E(\mathbf{R})=E\{\sum_i n_i\}-\sum_i E\{n_i\}, \qquad (3.12)$$

where the summation is carried out for all the ions, atoms, or molecules. The sum of the internuclear Coulomb interaction together with the electron-ion and Hartree electron-electron interactions in the case of neutral atoms is assumed to be zero and in the case of ions it is replaced by the Madelung energy of the ion-ion interaction. If we consider the cohesive energy as a function of the lattice parameters and approximate the resultant curve by simple phenomenological expressions for the pair interionic or interatomic interactions, we can find the parameters of this interaction from "first principles."

The first calculations of this type were made back in the thirties by Jensen, Lenz, and Gombaś (for a review of their work see Ref. 20). Some of the calculations made by this method in the case of crystals were reported also in the fifties and sixties (citations of the relevant work can be found in Ref. 65). The current round of such calculations began in 1970 with the work of Gaydaenko and Nikulin[66] who calculated interatomic interactions within the framework of the functional of Eq. (3.11). This method was developed further in later work[65,67-71] in which the exchange-correlation contribution to the energy was allowed for more accurately than in the exchange approximation and this was done using the interpolation formula for $\varepsilon_{\mathrm{xc}}(n)$ derived by Kim and Gordon[65] or in the local density approximation. Calculations were made of the cohesive energy, equilibrium interatomic distances, pressure at polymorphic transitions, elastic constants, etc. for a large number of ionic and molecular crystals, and the results were in good agreement with the available experimental data. The phonon spectra were not calculated. This was done in Refs. 72–75 in connection with the discussion of various types of lattice instability in ionic crystals: melting, transition to a superionic state, and structural instability.

This method suffers from a number of shortcomings: for example, the use of Eq. (3.10) for the kinetic energy, which is a very rough approximation,[60] and inconsistency of calculations of the electron density in the sense of the condition (3.6). More rigorous and consistent approaches have recently been developed for a calculation of the properties of the ground state of crystals and phonon spectra, which avoid these and some other shortcomings. We shall now consider such approaches.

We shall begin with a brief description of a more consistent approach to the density functional method put forward by Kohn and Sham.[58] The difficulties associated with the fact that the exact form of the kinetic energy functional is not

known were avoided by these authors by adding and subtracting from the functional of Eq. (3.7) the kinetic energy of noninteracting electrons with the same density $T_0\{n\}$

$$E\{n\} = T_0\{n\} + \int d\mathbf{r}\, n(\mathbf{r})\, V_{ext}(\mathbf{r})$$

$$+ \frac{e^2}{2} \int d\mathbf{r}\, d\mathbf{r}' \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}\{n\}. \qquad (3.13)$$

Here E_{xc} is the total exchange-correlation energy of the system

$$E_{xc}\{n\} = \tilde{E}_{xc}\{n\} + T\{n\} - T_0\{n\}.$$

Next, representation of the electron density in the form

$$n(\mathbf{r}) = \sum_i n_i \,|\varphi_i(\mathbf{r})|^2, \qquad (3.14)$$

where n_i are the occupancy numbers of single-particle states, equal to zero or unity, and minimization in accordance with Eq. (3.6) yields the following equations for the wave functions φ_i:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r}) \right) \varphi_i(\mathbf{r})$$

$$= E_i \varphi_i(\mathbf{r}); \qquad (3.15)$$

here, $V_{xc}(\mathbf{r})$ is the exchange-correlation potential

$$V_{xc}\{n(\mathbf{r})\} = \frac{\delta}{\delta n} E_{xc}\{n\}. \qquad (3.16)$$

We shall now rewrite Eq. (3.15) in the form

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U_{eff}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = E_i \varphi_i(\mathbf{r}); \qquad (3.17)$$

this yields the usual single-particle Schrödinger equation with the effective potential

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}). \qquad (3.18)$$

The total energy of the system of interacting electrons can be described as follows in terms of solutions of Eq. (3.17):

$$E\{n\} = \sum_i n_i E_i - \frac{e^2}{2} \int d\mathbf{r}\, d\mathbf{r}' \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$+ E_{xc}\{n\} - \int d\mathbf{r}\, n(\mathbf{r})\, V_{xc}(\mathbf{r}). \qquad (3.19)$$

The second and fourth terms appear in the above equation because, as usual, it is necessary to subtract the single-particle energies of the direct Coulomb and exchange-correlation interactions taken into account twice in the summation process. We shall not discuss in greater detail the Kohn-Sham method or the problem of construction of the exchange-correlation potential $V_{xc}\{n\}$ central to this method: readers interested in these topics can turn to Refs. 58 and 76–78, as well as to a book[61] and reviews.[59,60,79]

The Kohn-Sham method together with the energy relationships (3.13) and (3.19) and a suitable selection of the expression for the exchange-correlation functional E_{xc} [it is usual to employ the approximation of the local density and the results of calculations of $\varepsilon_{xc}(n)$ for a homogeneous electron gas] makes it possible to carry out, in principle, a self-consistent *ab initio* calculation of the properties of the ground state of a crystal, including the energy and electron density. Such a self-consistent calculation procedure is described in a review in Ref. 80.

We shall now consider in greater detail the problem of calculation of the phonon spectra of nonmetallic crystals from first principles. Two calculation methods are available at present: a direct method of "frozen-in" phonons[80–82] and a dielectric method based on exact microscopic expressions for the force matrix.[51–53] Both approaches use the density functional to calculate the energy of the ground state for a given configuration of nuclei in the first case and the static electron susceptibility in the second case.

The method of frozen-in phonons involves direct construction (calculation) of the adiabatic potential in which nuclei are moving. This is done by finding the total energy of the ground state of the system when the lattice is undistorted and also in the presence of a distortion representing one of the normal lattice vibrations; the difference between them is then found as a function of the distortion parameters. This yields not only the frequencies of normal vibrations in the harmonic approximation, but also the parameters representing the anharmonicity of the lattice vibrations.[80–83] In recent years this method has been used on several occasions to calculate the phonon spectra of several semiconductors and metallic crystals.[80–86] It is particularly interesting to consider calculations carried out from first principles, without any fitting parameters and specifying only the charges and masses of the nuclei and the type of the crystal structure (interatomic distances for an equilibrium configuration of nuclei are also determined in the process of calculation).[80,82–85] The precision of such calculations is unexpectedly high[80] in spite of the number of approximations made: the calculated values of the cohesive energy, lattice constants, elastic constants, and phonon frequencies differ from the experimental values by about 1% or less. By way of example, we shall give the results of a calculation carried out in the case of silicon and germanium.[84] It is clear from Eq. (3.13) describing the energy functional that the quantity $\omega^2(\mathbf{q})$, where $\mathbf{q}$ is the wave vector, can be represented as a sum of the following contributions:

$$\omega^2(\mathbf{q}) = \omega_{ii}^2 + \omega_e^2, \qquad \omega_e^2 = \omega_{kin}^2 + \omega_{ei}^2 + \omega_H^2 + \omega_{xc}^2, \qquad (3.20)$$

where ω_{ii}^2 is the contribution of the interionic interactions (core-core interactions); ω_e^2 is the total contribution of the valence electrons which consists of ω_{kin}^2 representing the kinetic energy of electrons and ω_{ei}^2 which is due to the interaction of electrons with the ion cores, and ω_H^2 and ω_{xc}^2 representing the Hartree and exchange-correlation contributions to the Coulomb interaction between the valence electrons. Table I gives the values of the moduli[84] corresponding to Eq. (3.20):

$$\varkappa^2 = 2\frac{\Delta E(\mathbf{U}^q)}{|\mathbf{U}^q|^2},$$

where $\mathbf{U}^q$ is the normal coordinate, for the optical vibrations of the lattice at the point Γ and for the transverse acoustic vibrations at the boundary of the zone at the point X in the case of germanium and silicon. It is clear from this table that many of the partial contributions to the phonon frequencies are large in the absolute sense and generally speaking are of the order of the phonon frequency itself or even greater than this frequency. This shows that the problem of "soft" lattice

TABLE I. Contributions to force constants of phonons at points Γ and X and values of $2a(c_{11} - c_{12})$ obtained for silicon and germanium.[84] (All results are in units of $eV/\text{Å}^2$—see also explanations in text).

	Si			Ge		
	LTO (Γ)	TA (X)	$2a(c_{11} - c_{12})$	LTO (Γ)	TA (X)	$2a(c_{11} - c_{12})$
k_{kin}	30,88	−17,49	−8,58	16,40	−10,76	−6,43
k'_{ei}	−72,28	58,06	57,99	−38,27	45,72	49,86
k_H	26,98	−19,39	−19,25	3,11	−15,64	−18,10
k_{xc}	−7,30	6,19	5,25	−0,40	4,67	4,81
k_e	−21,82	27,38	35,40	−19,15	23,99	3ˑ,13
k'_{ii}	48,26	−25,11	−28,14	42,70	−22,22	−24,90
k_{tot}	26,44	2,27	7,26	23,55	1,77	5,23
k_{tot}^{exp}	27,75	2,32	6,96	24,73	1,71	5,79

vibration modes in crystals is very far from simple, because the formation of a phonon spectrum results in a fairly accurate compensation of the various contributions. Moreover, we can see from calculations of the transverse acoustic mode at the zone edge [TA(X)] that the electron contribution to this mode becomes stabilizing ($\omega_e^2 > 0$), in contrast to the simplest models in which the electron contribution is always regarded as destabilizing.

The above method of frozen-in phonons is in principle valid only when we are dealing with normal modes characterized by a wave vector q comparable with any reciprocal lattice vector, because only then does the distorted structure remain periodic and two single-particle equations (3.15) and (3.16) can be solved. A new cell of the distorted structure should not be too large (it should not contain too many atoms).[81] Some difficulties are encountered also in calculations of phonon spectra of polar crystals made by this method and this is due to a macroscopic field which appears in the case of longitudinal optical vibrations.[86] However, we shall not discuss these topics and confine ourselves to a reference to a book[83] and a review[82]; we shall instead describe the most universal method for the calculation of phonon spectra in crystals based on the results of Refs. 50–53, in which these difficulties are not encountered.

The essence of the method is direct calculation of the change in the energy of the electron system δE by a standard many-body theory of perturbations from the change in the nuclear-electron interaction $\delta V_n (\mathbf{r})$ associated with the displacements of nuclei from the equilibrium positions. It is shown in Refs. 50–53 that the change in the electron energy could be expressed, in the second order in respect of the displacements U_s^R, using the longitudinal microscopic susceptibility of electrons $\chi(\mathbf{r}, \mathbf{r}')$ which describes the linear response of the electron density to a change in the external potential

$$\delta\rho_e (\mathbf{r}) = \hat{\chi}\delta V_{eff} = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \delta V_{eff} (\mathbf{r}'). \quad (3.21)$$

Including in the electron Hamiltonian the terms of the first and second order in respect of the displacements, we can describe the change in the potential by

$$\delta V_n = \delta V_n^1 + \delta V_n^2. \quad (3.22)$$

Then, the change in the energy, accurate to the second order with respect to U_s^R, can be written in the form[50-53]

$$\delta E^2 = \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}' \delta V_n^1 (\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}') \delta V_n^1 (\mathbf{r}') + \delta \tilde{E}^2, \quad (3.23)$$

where the term $\delta\tilde{E}^2$ appears because of inclusion of the term δV^2 in the first order of perturbation theory. It can also be expressed in terms of the susceptibility $\chi(\mathbf{r}, \mathbf{r}')$ but we shall not do this for lack of space. It is important to note that this term guarantees the translational invariance of the quantity δE^2, because in the case of displacements of nuclei as a whole ($U_s^R = \text{const}$) the change in the energy vanishes.

The change in the energy δE^2 written in the form of Eq. (3.23) has a simple physical meaning and represents just the energy of the Coulomb interaction of the excess electron charge $\delta\rho_e$ which appears under the influence of a change in the potential δV_n. In the case of polar crystals the change δE^2 contains parts which diverge for $U_s^R = \text{const}$. Similar diverging terms occur also in the contribution of the internuclear interaction. Singular contributions should be separated and analyzed individually[51,52] bearing in mind that the sum of these contributions again obeys the condition of translational invariance. We shall discuss this problem in greater detail later.

The phonon spectrum of a crystal could be determined in the harmonic approximation if we know the dynamic matrix

$$\hat{D}_{st} (\mathbf{q}) = \frac{\hat{\Phi}_{st} (\mathbf{q})}{(M_s M_t)^{1/2}}, \quad (3.24)$$

where $\hat{\Phi}(\mathbf{q})$ is the force matrix representing the lattice Fourier transform of the matrix of the second derivatives with respect to the total energy of the system along the coordinates of the nuclei $\hat{\Phi}(\mathbf{R}\text{-}\mathbf{R}')$ and

$$\hat{\Phi}_{st} (\mathbf{q}) = \sum_{\mathbf{R}'} \exp\left[i\mathbf{q}(\mathbf{R} - \mathbf{R}' + \mathbf{R}_s - \mathbf{R}_t)\right] \Phi_{st} (\mathbf{R} - \mathbf{R}'). \quad (3.25)$$

The electron contribution to the force matrix can be written as follows[49-53]:

$$\Phi_{si, tj}^E (\mathbf{R} - \mathbf{R}') = X_{si, tj} (\mathbf{R} - \mathbf{R}')$$
$$- \delta_{\mathbf{R}\mathbf{R}'}\delta_{st} \sum_{\mathbf{R}'', U} X_{si, uj} (\mathbf{R} - \mathbf{R}''), \quad (3.26)$$

where

$$X_{si, tj} (\mathbf{R} - \mathbf{R}')$$
$$= Z_s^n Z_t^n e^2 \int d\mathbf{r}\, d\mathbf{r}' \frac{\partial}{\partial x_i} v_c (\mathbf{r} - \mathbf{R} - \mathbf{R}_s) \chi(\mathbf{r}, \mathbf{r}')$$
$$\times \frac{\partial}{\partial x_j'} v_c (\mathbf{r}' - \mathbf{R}' - \mathbf{R}_t). \quad (3.27)$$

The contributions of $\delta\hat{V}_{ne}^{(1)}$ and $\delta\hat{V}_{ne}^{(2)}$ to the force matrix are not independent and, moreover, we can see from Eq. (3.26) that they can be expressed in terms of the same quantity $\chi_{si,tj}$ $(\mathbf{R} - \mathbf{R}')$.

Equations (3.24)–(3.27) demonstrate that in order to calculate the electron contribution to the force matrix in the adiabatic approximation, we have to know the static electron susceptibility[4] $\chi(\mathbf{r}, \mathbf{r}'; \omega = 0)$. Going over to the momentum representation, we find that after allowance for the periodicity of a crystal the susceptibility $\hat{\chi}$ is transformed into a matrix in terms of the reciprocal lattice vectors $\mathbf{K}$ and $\mathbf{K}'$, which is diagonal in respect of the reduced wave vector $\mathbf{q}$, that vary within the first Brillouin zone

$$\chi(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{K}, \mathbf{K}'} \int \frac{d^3q}{(2\pi)^3} \exp[i(\mathbf{q}+\mathbf{K})\,\mathbf{r}]\,\chi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$$

$$\times \exp[-i(\mathbf{q}+\mathbf{K}')\,\mathbf{r}']. \qquad (3.28)$$

In principle, the matrix $\chi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ can be calculated either using the conventional many-body theory or employing the density functional method (we recall that we are talking of the static permittivity). With this in mind, specifying a small change in the external potential δV_{ext} in the Schrödinger equation (3.17), using the Kohn-Sham method, and applying Eq. (3.14), we can use conventional perturbation theory to find the corresponding change in the electron charge density and thus deduce the electron susceptibility.

We have employed so far the harmonic approximation in the description of lattice dynamics and this is usually sufficient for discussing the lattice stability at $T = 0$ K. However, many properties, such as stabilization of the critical TO vibrations above T_c and the structure of the low-temperature phase, are governed entirely by the anharmonicity of lattice vibrations.[5] The usual description of the anharmonic effects in crystals is based on the following phenomenological lattice Hamiltonian[5]

$$\hat{H}_{ph} = \hat{H}_{ph}^{(0)} + \hat{V}_{int}, \qquad \hat{V}_{int} = \hat{V}_3 + \hat{V}_4 + \ldots, \qquad (3.29)$$

where, for example,

$$\hat{V}_3 = \frac{1}{3!}\,\Phi_{\alpha\beta\gamma}^{(3)}\,\hat{U}_\alpha\hat{U}_\beta\hat{U}_\gamma. \qquad (3.30)$$

$\alpha \equiv (\mathbf{R}, \mathbf{R}_{s,i})$ and $\hat{U}_{si}^{\mathbf{R}}$ is the operator representing displacements of the nuclei $(\mathbf{R}, \mathbf{R}_s)$. The tensors of the anharmonic coefficients $\hat{\Phi}^{(m)}$ are derivatives of the adiabatic potential $V_{ad} = V_{nn} + E_0\{\mathbf{R}\}$ of the mth order in respect of the displacements of nuclei. The electron contribution to $\hat{\Phi}^{(m)}$ can be found in the same way as the contribution to the force matrix $\hat{\Phi} \equiv \hat{\Phi}^{(2)}$, using exact microscopic expressions for the change in E_0 in the mth order with respect to $\mathbf{U}_{si}^{\mathbf{R}}$.

An analysis[53] shows that, in contrast to the force matrix $\hat{\Phi}^{(2)}$ the microscopic expressions for the electron contribution to $\hat{\Phi}^{(3)}$ and $\hat{\Phi}^{(4)}$ contain nonlinear susceptibilities which occur in the expressions for $\delta\rho_e^{(2)}$ and $\delta\rho_e^{(3)}$ (Ref. 54). The microscopic expressions for $\hat{\Phi}^{(3)}$ and $\hat{\Phi}^{(4)}$ have not been investigated as thoroughly as the expression for $\hat{\Phi}^{(2)}$ studied in Refs. 43 and 49–53. Some of the results were obtained by Meissner[54] for the effective dynamic matrix $\hat{\Gamma}$ [see Eq. (3.4)] within the framework of a self-consistent procedure allowing for the anharmonicity. In particular, it was shown in Ref. 54 that the corresponding effective force matrix has a structure similar to Eq. (3.26), which guarantees that the acoustic sum rule of Eq. (2.17) is obeyed.

These relationships are general and they apply to a system composed of stripped nuclei and all the electrons in a crystal. In specific calculations it is usual to consider a system of iron cores and all the valence electrons and to apply the method of a pseudopotential which is found either empirically or from first-principle calculations. Consequently, in Eqs. (3.23) and (3.27) instead of the potential of the nuclei, we have a pseudopotential for this type of atom, and instead of the total electron susceptibility, we have the susceptibility of valence electrons, which is naturally itself an approximation. However, it is assumed that the main difficulties are not due to this approximation but due to the problem of calculation of the electron susceptibility. In fact, with the exception of simple metals for which the off-diagonal elements of the polarization operator $\pi(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}')$ (see below) with $\mathbf{K} \neq \mathbf{K}'$ are small and can be included within the framework of perturbations involving a weak pseudopotential, whereas in other cases (particularly in the case of semiconductors and insulators) there is a greater number of Bloch bands and the dimensions of the matrices of the reciprocal lattice vectors are larger. For example, in the case of semiconductors with s and p electrons, in which case we can again introduce a pseudopotential description of the energy band structure, it is necessary to allow for 20–40 Bloch bands and up to 300 reciprocal lattice vectors. In spite of its complexity, the problem is not hopeless and progress has been made toward its solution (see Ref. 83), both in calculating the dispersion law of phonon frequencies in a wide range of wave vectors[87] and in calculation of the frequencies of optical lattice vibrations in the $\mathbf{q} = 0$ case.[88]

The most important advantage of the "dielectric" approach described above is that it can yield a series of exact and rigorous relationships for the dielectric response functions and for the force matrix of crystals of all types (metals, insulators, and semiconductors). All the specific features of the electron structure of a crystal are then contained in the electron susceptibility matrix $\hat{\chi}$. In accordance with the purpose of the present review we shall therefore consider in greater detail this approach and particularly the structure of the matrix $\hat{\chi}$ and the force matrix in the case of nonmetallic crystals. We shall be interested particularly in polar crystals, i.e., those in which dipole-active optical lattice vibrations are possible.

3.2. Lattice dynamics and dielectric properties of polar insulators and semiconductors

Polar crystals are those which are characterized by a finite macroscopic (transverse optical) charge tensor $\hat{Z}(s)$ see Eq. (2.4)]. In other words, in polar crystals among the long-wavelength optical lattice vibrations there are also dipole-active vibrations which are accompanied by the appearance of a long-wavelength (macroscopic) polarization $\mathbf{p}^q$ and a macroscopic field $\mathbf{E}^q$ resulting in the splitting of the LO and TO lattice vibrations. Polar crystals are above all ionic crystals, but there are also polar crystals with zero ionicity and familiar examples of these are graphite[89] and group VI elements (Se, Te).[90]

In developing a theory of lattice dynamics of polar insulators and semiconductors, we encountered difficulties associated with separation of the contribution of the macroscop-

ic field $\mathbf{E}^q$. In the model of point ions these difficulties are manifested by the formal divergence of some of the partition functions for a dipole lattice, resulting in nonanalytic behavior of the force matrix $\hat{\Phi}^I(\mathbf{q})$ in the limit $\mathbf{q} \to 0$ (Ref. 20). Separation of the regular part of the force matrix in the limit $\mathbf{q} \to 0$ can be made in this case by the Ewald method and the result is of the form[20]

$$\Phi^I_{si,\,tj}(\mathbf{q}) = e^2 \left[C_{si,\,tj}(\mathbf{q}) - \delta_{st} \sum_u C_{si,\,uj}(0) \right]$$
$$+ \frac{4\pi e^2}{v_0} \frac{q_i q_j}{q^2} Z_s Z_t \exp\left[i\mathbf{q}(\mathbf{R}_s - \mathbf{R}_t)\right], \qquad (3.31)$$

where

$$C_{si,\,tj}(\mathbf{q}) = Q_{si,\,tj}(\mathbf{q}) Z_s Z_t \exp\left[i\mathbf{q}(\mathbf{R}_s - \mathbf{R}_t)\right],$$

where $Z_s e$ are the ion charges, and $\hat{Q}(\mathbf{q})$ is regular in the limit $\mathbf{q} \to 0$ (the expression for $\hat{Q}$ is given in Ref. 20). Equation (3.31) describes also the contribution of stripped nuclei to the force matrix if we replace the charges of ions with the charges of the nuclei $Z_s^n e$.

The procedure of separation of the contribution of the macroscopic field to the electron part of the force matrix was first carried out in Refs. 51 and 52. In view of the importance of the results, we shall give the conclusion reached following mainly Ref. 51. We shall do this using the exact microscopic expressions (3.25)–(3.27) obtained earlier for the electron contribution to the force matrix. Adopting expansion in terms of the reciprocal lattice vectors [see Eq. (3.28)], we find that

$$\Phi^E_{si,\,tj}(\mathbf{q}) = X_{si,\,tj}(\mathbf{q}) - \delta_{st} \sum_u X_{si,\,uj}(0), \qquad (3.32)$$

where

$$X_{si,\,tj}(\mathbf{q}) = Z_s^n Z_t^n e^2 \exp\left[i\mathbf{q}(\mathbf{R}_s - \mathbf{R}_t)\right]$$
$$\times \sum_{\mathbf{K},\,\mathbf{K}'} \exp(i\mathbf{K}\mathbf{R}_s)(\mathbf{q}+\mathbf{K})_i v_c(\mathbf{q}+\mathbf{K})$$
$$\times \chi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') v_c(\mathbf{q}+\mathbf{K}')(\mathbf{q}+\mathbf{K}')_j \exp(-i\mathbf{K}'\mathbf{R}_t), \qquad (3.33)$$

$$v_c(\mathbf{q}+\mathbf{K}) = \frac{4\pi}{v\,|\mathbf{q}+\mathbf{K}|^2}.$$

We shall now consider in greater detail the properties of the matrix $\chi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$. The electron susceptibility operator χ describes the linear response of the charge density of electrons in the system to a change in the external field:

$$\delta\rho_e^{(1)}(\mathbf{r}) = \hat{\chi}\delta V_{\text{ext}} \equiv \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \delta V_{\text{ext}}(\mathbf{r}'). \qquad (3.34)$$

We shall also introduce a polarization operator $\hat{\pi}$ describing the linear reaction of the density of the electron charge to a change in the total acting field $\delta V_{\text{tot}}^{(1)}$ and we shall also use an operator describing the longitudinal microscopic electron permittivity $\hat{\varepsilon}$:

$$\delta\rho_e^{(1)}(\mathbf{r}) = \hat{\pi}\delta V_{\text{tot}}^{(1)} \equiv \int d\mathbf{r}' \pi(\mathbf{r}, \mathbf{r}') \delta V_{\text{tot}}^{(1)}(\mathbf{r}'), \qquad (3.35)$$

$$\delta V_{\text{tot}}^{(1)}(\mathbf{r}) = \hat{\varepsilon}^{-1}\delta V_{\text{ext}} \equiv \int d\mathbf{r}' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}') \delta V_{\text{ext}}(\mathbf{r}'), \qquad (3.36)$$

where $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}')$ is the kernel of the operator which is the inverse of $\hat{\varepsilon}$. Bearing in mind that

$$\delta V_{\text{tot}}^{(1)}(\mathbf{r}) = \delta V_{\text{ext}} + \hat{v}_c \delta\rho_e^{(1)} \equiv \delta V_{\text{ext}} + \int d\mathbf{r}' v_c(\mathbf{r}-\mathbf{r}') \delta\rho_e^{(1)}(\mathbf{r}'), \qquad (3.37)$$

we obtain relationships between $\hat{\chi}$, $\hat{\varepsilon}$, and $\hat{\pi}$, which in the $\mathbf{K}$ representation are of the form

$$\chi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = \pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$$
$$+ \sum_{\mathbf{K}''} \pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}'') v_c(\mathbf{q}+\mathbf{K}'') \chi(\mathbf{q}+\mathbf{K}'', \mathbf{q}+\mathbf{K}'),$$

$$\varepsilon(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = \delta_{\mathbf{K},\mathbf{K}'} - v_c(\mathbf{q}+\mathbf{K})\pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}'),$$
$$\qquad (3.38)$$

$$\varepsilon^{-1}(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = \delta_{\mathbf{K},\mathbf{K}'} + v_c(\mathbf{q}+\mathbf{K})\chi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}').$$

We can see from the first relationship in the system (3.38) that the expression for χ includes contributions of long-wavelength Fourier components of the interaction $v_c(\mathbf{q})$, which are singular at $\mathbf{q} \to 0$ and contribute to the macroscopic field. Exclusion of these contributions from χ gives a quantity $\tilde{\chi}$ satisfying the equation

$$\tilde{\chi}(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = \pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$$
$$+ \sum_{\mathbf{K}''\neq 0} \pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}'') v_c(\mathbf{q}+\mathbf{K}'') \tilde{\chi}(\mathbf{q}+\mathbf{K}'', \mathbf{q}+\mathbf{K}').$$
$$\qquad (3.39)$$

Solving simultaneously Eqs. (3.38) and (3.39), we can express the Fourier component of the matrix χ and terms of $\hat{\chi}$ and separate the term with a nonanalytic contribution of the long-range macroscopic field[51]

$$\chi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$$
$$= \tilde{\chi}(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') + \tilde{\chi}(\mathbf{q}+\mathbf{K}, \mathbf{q}) \frac{V_c(\mathbf{q})}{\varepsilon^m(\mathbf{q})} \tilde{\chi}(\mathbf{q}, \mathbf{q}+\mathbf{K}'),$$
$$\qquad (3.40)$$

where $\varepsilon^m(\mathbf{q})$ is known as the macroscopic permittivity given by the relationship

$$(\varepsilon^m(\mathbf{q}))^{-1} = \varepsilon^{-1}(\mathbf{q}, \mathbf{q}) = 1 + V_c(\mathbf{q})\chi(\mathbf{q}, \mathbf{q}). \qquad (3.41)$$

Using Eq. (3.57), we can write down $\varepsilon^m(\mathbf{q})$ in the following form:

$$\varepsilon^m(\mathbf{q}) = 1 - V_c(\mathbf{q})\tilde{\chi}(\mathbf{q}, \mathbf{q}). \qquad (3.42)$$

Separating from Eq. (3.33) the terms with $\mathbf{K}$ and $\mathbf{K}'$ when they vanish and substituting Eq. (3.40) in (3.33), we find that simple transformations yield the following expression for the total force matrix:

$$\Phi_{si,\,tj}(\mathbf{q}) = \Phi^I_{si,\,tj}(\mathbf{q}) + \Phi^E_{si,\,sj}(\mathbf{q}). \qquad (3.43)$$

or

$$\Phi_{si,\,tj} = \overline{\Phi}_{si,\,tj}(\mathbf{q}) - \delta_{st} \sum_U \overline{\Phi}_{si,\,uj}(0)$$
$$+ e^2 \exp\left[i\mathbf{q}(\mathbf{R}_s - \mathbf{R}_t)\right]$$
$$\times \left[(Z_s^n q_i + A_i^\dagger(s, \mathbf{q})) \frac{V_c(\mathbf{q})}{\varepsilon^m(\mathbf{q})} (Z_t^n q_j + A_j(t, \mathbf{q})) \right], \qquad (3.44)$$

where

$$A_i^\dagger(s, \mathbf{q}) = Z_s^n \sum_{\mathbf{K}\neq 0} e^{i\mathbf{K}\mathbf{R}_s}(\mathbf{q}+\mathbf{K})_i V_c(\mathbf{q}+\mathbf{K}) \tilde{\chi}(\mathbf{q}, \mathbf{q}+\mathbf{K})$$
$$\qquad (3.45)$$

and $\overline{\Phi}_{si,tj}(\mathbf{q})$ describes the contribution to the force matrix which is analytic in the limit $\mathbf{q} \to 0$. The electron component of this contribution is given by Eq. (3.33) when the matrix χ and replaced with χ' and summation is carried out only over values of $\mathbf{K}$ and $\mathbf{K}'$ which are not equal to zero.

The expressions (3.44)–(3.45) are general and valid

both for insulators and metals.[91] The differences appear only when we go over to the long-wavelength limit and are associated with the fact that the quantities $\bar{\chi}(\mathbf{q}, \mathbf{q})$, $\chi(\mathbf{q} + \mathbf{K}, \mathbf{q})$, $\chi(\mathbf{q}, \mathbf{q} + \mathbf{K})$, and $\varepsilon^m(\mathbf{q})$ behave differently in the limit $\mathbf{q} \to 0$ for metals and insulators.

It is shown in Refs. 51 and 52 that the following equality applies in the case of insulators:

$$q_i Z_s^n + A_i\,(s,\,q) = q_j Z_{ij}\,(s), \qquad (3.46)$$

where $\hat{Z}(s)$ is the macroscopic (transverse acoustic) charge tensor for the system, defined above [see Eq. (2.4)]. Using Eqs. (3.44) and (3.45), we obtain the following expression for the total force matrix in the range of low values of $\mathbf{q}$ (Refs. 51 and 52):

$$\hat{\Phi}_{st}\,(q \to 0) = \hat{\Phi}_{st}\,(0) - \delta_{st} \sum_V \hat{\Phi}_{su}\,(0) + \hat{Z}^+\,(s)\,\frac{4\pi e^2}{V_0 \varepsilon_\infty}\,P^L \hat{Z}\,(t),$$
$$(3.47)$$

$$P_{ij}^L = \frac{q_i q_j}{q^2}\,,$$

where $\varepsilon_\infty = \lim_{q \to 0} \varepsilon^m(\,q_1)$ and the exact microscopic expression for $\hat{Z}(s)$ is

$$Z_{ij}\,(s) = Z_s^n \delta_{ij} + Z_s^n \sum_{K \neq 0} e^{-i\mathbf{K}\mathbf{R}_s} k_i V_c\,(k)\,\tilde{\chi}_j^1\,(0,\,\mathbf{K}). \quad (3.48)$$

The second term in Eq. (3.48) can be written down using the asymptotic behavior of the matrix $\bar{\chi}(\mathbf{q} + 0, \mathbf{q} + \mathbf{k})$ at low values of $\mathbf{q}$:

$$\tilde{\chi}\,(\mathbf{q} + 0,\ \mathbf{q} + \mathbf{k}) = q_j \tilde{\chi}^i\,(\mathbf{q} + 0,\ \mathbf{q} + \mathbf{k}). \qquad (3.49)$$

Moreover, it is shown in Refs. 51 and 52 that the charge $\hat{Z}_s$ governed by Eq. (3.48) satisfies the condition

$$\sum_s Z_{ij}\,(s) = 0 \qquad (3.50)$$

and thus demonstrates that the acoustic sum rule is satisfied by the complete force matrix of Eq. (2.17).

Applying the phenomenological relationships of Eq. (2.4) and the expression (3.44) for $\hat{\Phi}(\,q)$ at low values of q,

we obtain the following general expression for the low-frequency permittivity tensor of a crystal (see Footnote 3):

$$\varepsilon_{ij}\,(\omega \to 0) = \varepsilon_\infty^{ij} + \frac{4\pi e^2}{v_0} \sum_{s,\,t} \{\hat{Z}\,(s)\,[\bar{\Phi}^{-1}\,(0)]_{st}\,\hat{Z}\,(t)\}^{ij}. \quad (3.51)$$

We shall discuss the results obtained in the case of diatomic cubic crystals. The tensor $\hat{Z}_s$ is then proportional to a unit tensor and we can introduce a scalar macroscopic charge (Born charge)

$$Z_{ij}\,(s) = Z_s \delta_{ij}, \quad \sum_s Z_s = 0, \quad Z = |\,Z_s\,| \quad (s = 1,\,2). \quad (3.52)$$

The frequencies of optical lattice vibrations are described by

$$\omega_{LO}^2 = \omega_{TO}^2 + \frac{Z^2}{\varepsilon_\infty}\,\Omega^2, \quad \Omega^2 = \frac{4\pi e^2}{\mu v_0}\,, \qquad (3.53)$$

$$\omega_{TO}^2 = \frac{1}{\mu}\left(\frac{4\pi e^2}{3\mu v_0}\,Z_1^n Z_2^n - S_{12}\right), \qquad (3.54)$$

where μ and v_0 are the reduced mass and the unit-cell volume, and we have

$$S_{12} = \frac{e^2}{3}\,Z_1^n Z_2^n \sum_{\mathbf{K},\,\mathbf{K}' \neq 0} \exp\,[i\,(\mathbf{K}\mathbf{R}_1 - \mathbf{K}\mathbf{R}_2)]$$
$$\times\,(\mathbf{K}\mathbf{K}')\,v_c\,(\mathbf{K})\,\tilde{\chi}\,(\mathbf{K},\,\mathbf{K}')\,v_c\,(\mathbf{K}'), \quad (3.55)$$

whereas in the case of the low-frequency permittivity ε_0, we find that

$$\varepsilon_0 = \varepsilon_\infty + Z^2\,\frac{\Omega^2}{\omega_{TO}^2} = \frac{\omega_{LO}^2}{\omega_{TO}^2}\,\varepsilon_\infty. \qquad (3.56)$$

The last equation (representing the Lyddane-Sachs-Teller relationship) is obtained using Eq. (3.53) for ω_{LO}^2.

The relationships obtained apply to a system composed of stripped nuclei and all the electrons in a crystal. When the relationships are applied to a system composed of stripped ion cores and valence electrons, which are usually employed in specific calculations, the potential of the nuclei must then be replaced with the potentials of the corresponding ion cores and the total electron susceptibility $\bar{\chi}$ should be replaced with the susceptibility of the valence electrons.

TABLE II. Results of calculations of frequencies of TO(Γ) phonons, total electron contribution $\tilde{\omega}_c^2$, frequencies of TO vibrations found allowing only for the diagonal terms of the polarization operator $(\tilde{\omega}_{TO}^2)_d$, contributions of off-diagonal components of the polarization operator $\tilde{\omega}_c^2$, denoted by $(\tilde{\omega}_c^2)_{nd}$, and of relative error in the calculation of $\tilde{\omega}_c^2$ denoted by $\delta\omega_c^2$ (Refs. 36 and 88). Explanations in text. All quantities are given in units of $\Omega^2 = 4\pi e^2/v_0$. In the case of SnTe and GeTe the calculations were made for the cubic phase at $T = 0$ K. For GeTe in the column $(\tilde{\omega}_{TO}^2)_{exp}$ the values in parentheses are calculated from the relative error $\delta\omega_c^2$ and the values of ω_{TO}^2 and ω_c^2 computed in Ref. 36.

	$\tilde{\omega}_{ii}^2 = \frac{Z_a Z_c}{3}$	$\tilde{\omega}_e^2$	$\tilde{\omega}_{TO}^2$		$(\tilde{\omega}_{TO}^2)_d$	$(\tilde{\omega}_e^2)_{nd}$	$\delta\omega_e^2$
			theory	experiment			
Si [88]	5,3	—1,523	3,81	3,09	3,994	—0,18	0,47
Ge [88]	5,3	—2,88	2,46	3,12	3,17	—0,71	0,23
GaAs [88]	5	—2,94	2,06	2,40	3,22	—1,16	0,12
ZnSe [88]	4	—3,15	0,85	1,36	3,21	—2,35	0,16
GaP [36]	5	—2,54	2,46	2,37	2,97	—0,51	0,04
PbS [36]	8	—10,92	—2,92	0,14	1,46	—4,38	0,28
PbSe [36]	8	—11,24	—3,24	0,10	0,93	—4,17	0,30
PbTe [36]	8	—10,69	—2,68	0,04	1,42	—4,10	0,25
SnTe [36]	8	—11,34	—3,34	—0,06	1,62	—4,96	0,24
GeTe [36]	8	—11,76	—3,76	(—0,06)	1,12	—4,88	0,30
				(—0,23)			0,25
				(—0,82)			0,20
				(—1,41)			

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Microscopic calculations of the frequencies of optical lattice vibrations and of the macroscopic charge in cubic diatomic semiconductors were made in Refs. 36 and 88 using Eqs. (3.53)–(3.55). The results of the calculations of ω_{TO}^2 are presented in Table II. All the quantities are given in units of $\Omega^2 = 4\pi e^2/\mu v_0$. The theoretical value of ω_{TO}^2 is a sum of the contribution of ion cores ω_{ii}^2 and of the contributions of the valence electrons ω_e^2. In the case of crystals with the diamond and zinc-blende structures the agreement with the experimental values of ω_{TO}^2 is satisfactory. This is not true of IV–VI compounds (with the NaCl-type structure). Calculations[36] greatly overestimate the contribution of electrons to ω_{TO}^2, predicting a strong instability of TO vibrations in the NaCl structure of all five compounds. It was assumed in Ref. 36 that the calculations of ω_e^2 were inaccurate because of the neglect of the spin-orbit interaction and nonlocality of the pseudopotential. Another source of inaccuracy of the calculations of ω_e^2 is the use of the Hartree (random phase) approximation to describe the electron response in Refs. 88 and 36, i.e., the neglect of the exchange-correlation contribution to $\bar{\chi}$. It is clear from Table II that the relative error in the calculations

$$\delta_{\omega_e^2} = |(\omega_{TO}^2)_{theor} - (\omega_{TO}^2)_{exp}| \omega_e^{-2}$$

is of the same order of magnitude (~ 20–30%) in almost all the calculations, but in the case of IV–VI compounds this error is too large because ω_e^2 is high.

A detailed analysis of the influence of various elements of the matrix $\pi(\mathbf{K}, \mathbf{K}')$ on the value of ω_{TO}^2 is made in Ref. 88 for Si, Ge, GaAs, and ZnSe. It was found that when the matrix $\bar{\chi}(\mathbf{K}, \mathbf{K}')$ was of sufficiently large dimensions, the inclusion of the off-diagonal components of $\hat{\pi}$ with $\mathbf{K} \neq \mathbf{K}'$ in Eq. (2.70) lowered the frequency of TO vibrations. In the case of nonpolar Si and Ge crystals inclusion of such off-diagonal components of $\hat{\pi}$ had no significant influence on the value of ω_{TO}^2, whereas in the case of the polar compound ZnSe exhibiting strong ionicity the inclusion of off-diagonal components of $\hat{\pi}$ reduced considerably the frequency of the TO vibrations. These conclusions are supported by the results of Ref. 36 obtained for strongly polar IV–VI compounds for which the contribution of the off-diagonal components of $\hat{\pi}$ represents about 40% of the total electron contribution ω_e^2. These calculations demonstrate also that the off-diagonal contribution to ω_{TO}^2 is governed not by the ionicity but by the polarity of the compounds, since IV–VI compounds have an anomalously large macroscopic charge Z and a low ionicity. The relationship between the polarity and ionicity of diatomic cubic crystals is discussed in detail in the next section of the present review. The results of calculations of ω_{TO}^2 carried out ignoring the off-diagonal components of $\hat{\pi}$ and also the contribution of the off-diagonal components of $\hat{\pi}$ and ω_e^2 are given in Table II [they are denoted by $(\omega_{TO}^2)_d$ and $(\omega_e^2)_{nd}$, respectively].

3.3 Analysis of microscopic theories of ferroelectric instability in crystals

The exact microscopic expressions for the force matrix $\hat{\Phi}$, for the macroscopic charge sensor $\hat{Z}(s)$ and for ε_∞ found above allow us to go beyond the traditional model analysis of the lattice dynamics and the problem of structural instability of crystals. We shall now consider systematically the exist-

ing approaches to the problem of the ferroelectric instability treated from the point of view of the microscopic theory of lattice dynamics.

We shall begin with the classical theory of ferroelectricity which relates the lattice instability to dipole forces that appear as a result of long-wavelength optical displacements of nuclei from equilibrium positions in the paraelectric phase. In the simple ion picture the electron contribution to the induced dipole moment consists of the displacement of an ion as a whole (contribution of the ion charge) and of the displacements of electrons relative to the ion cores (contribution of the ion polarizabilities). This implies inclusion of only internal ion excitations in the description of the electron contribution to ε_∞ and to lattice dynamics of ionic crystals, whereas the contribution of ion-ion excitations is ignored. In reality, both internal ion and ion-ion excitations are important in ionic crystals. In the case of insulators such as alkali halide crystals, the contributions of the two types of excitation to, for example, ε_∞ are comparable.[92] On the other hand, in polar semiconductors the ion-ion excitations typically predominate and these correspond to characteristic interband transitions dominating ε_∞. For example, according to Ref. 93, the main contribution to ε_∞ of IV–VI compounds is made by transitions between P states of A and B atoms and the contribution of internal atomic excitations is small. The transfer of charge between ions associated with ion-ion excitations[92] results in a deviation from the simple ion picture of the polarized state of a crystal. This deviation increases on reduction in the average band gap and on increase in ε_∞, and is manifested by a large (compared with the ion charge) magnitude of the macroscopic Born charge Z of polar semiconductors.[34] Similar ideas were put forward earlier by Lucovsky, Martin and Burstein,[34,35] who demonstrated that in the case of polar semiconductors a considerable contribution to the induced dipole moment comes from excitation of the charge density of the valence electrons localized in a region of size r_0 exceeding the interatomic distance a_0, i.e., excitations which can be regarded as of the internal ion type. It also means that the actual parameter of the multipole expansion for polar semiconductors is $\sim r_0/a_0 \gtrsim 1$.

Bearing these points in mind, we can separate the excitations of the charge density of the valence electrons into localized (identifying them with internal electron transitions within ions) and delocalized corresponding to ion-ion transitions. We can describe localized excitations using a model of polarizable ions and the dipole approximation. Then, their contribution to ε_∞ (which we shall denote by ε_∞^{loc}) is described by the Lorenz-Lorentz formula and the contribution to Z and ω_{DD}^2 is described by Eqs. (2.20)–(2.23), where ε_∞ is replaced with ε_∞^{loc}. On the other hand, the model of polarizable ions and the dipole approximation are completely unsuitable for the description of delocalized states which, according to Refs. 21, 34, 35, 92, and 93, dominate the contributions to ε_∞ and Z.

It is however possible to consider the influence of the dipole-dipole interaction on dielectric properties and lattice dynamics of nonmetallic crystals without considering the concept of ions at all.[94] The above exact microscopic expressions for $\hat{\Phi}(\mathbf{q})$, $\hat{Z}(s)$, and ε_∞ and the method of multipole expansion for crystals[95] can be used to show that separation of the contribution of the dipole-dipole interaction gives re-

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lationships similar to Eqs. (2.5) and (2.20)–(2.23), and we can obtain exact microscopic expressions for the parameters representing the dipole-dipole interaction in crystals. Details of this procedure are described earlier by one of the present authors.[94] The idea behind this derivation is as follows. The above microscopic expressions for $\hat{\Phi}(q)$, $\hat{Z}(s)$ and ε_∞ contain a polarization operator $\hat{\pi}$, which carries all the quantum-mechanical information on the linear electron response of the system and on the direct Coulomb electron-nuclear and electron-electron interactions. Separation of specific components $v_c(q)$ in the limit $q\to 0$ for the direct Coulomb interaction, which contribute to the macroscopic field, is equivalent to separation of the nonanalytic part of the dipole-dipole interaction in the same limit $q\to 0$ (Ref. 94). In the case of the direct electron-electron Coulomb interaction this procedure corresponds to a change from χ to $\bar{\chi}$ [see Eqs. (3.39) and (3.40)]. The regular part of the dipole-dipole interaction (internal field) remains unseparated from the direct Coulomb interaction and, in particular, it is not separated from the external Coulomb forces contributing to $\bar{\chi}$ and is contained in the short-wavelength Fourier components $v_c(q + K)$ with $K\neq 0$. Using the method of multipole expansion for crystals,[95] we can separate explicitly the contribution of the regular part of the dipole-dipole interaction to ε_∞, $\hat{Z}(s)$, and $\hat{\Phi}(q)$ (Ref. 94). In the case of ε_∞ of arbitrary cubic crystals and for the macroscopic charge Z and the dipole contribution ω_{DD}^2 to the square of the frequency of TO lattice vibrations in diatomic cubic crystals the separation of the distribution of the internal field gives rise to a pole structure of the expressions for these quantities, exactly as in the model of polarizable ions

$$\varepsilon_\infty = 1 + \frac{(4\pi/v_0)\,\alpha^e}{1-(4\pi/3v_0)\,\alpha^e}\,,$$

$$Z = \frac{Z^i}{1-(4\pi/3v_0)\,\alpha^e}\,, \qquad (3.57)$$

$$\omega_{DD}^2 = \frac{(Z^i)^2}{1-(4\pi/3v_0)\,\alpha^e}\frac{\Omega^2}{3}\,, \qquad \Omega^2 = \frac{4\pi e^2}{\mu v_0}\,,$$

where α^e is the effective electron polarizability and Z^i is the effective ion charge (exact analog of the Szigeti charge[96]). The exact microscopic expressions for these quantities are also obtained in Ref. 94. It should be pointed out that if we ignore the renormalization of α^e because of the multipole contributions of higher orders, the microscopic expression obtained in Ref. 94 for α^e in the tight-binding approximation reduces to the corresponding expression obtained by Maksimov and Mazin,[97] whereas in the random phase approximation it reduces to the expression for α^e obtained by Adler.[95]

Eliminating α^e from the expressions for Z and ω_{DD}^2, we obtain

$$Z = \frac{\varepsilon_\infty + 2}{3}\,Z^i\,,$$

$$\omega_{DD}^2 = (\varepsilon_\infty + 2)\left(\frac{Z^i}{3}\right)^2\Omega^2. \qquad (3.58)$$

Finally, excluding Z^i from the expression for ω_{DD}^2, we find that

$$\omega_{DD}^2 = \frac{Z^2}{\varepsilon_\infty + 2}\Omega^2. \qquad (3.59)$$

Therefore, the contribution of the dipole-dipole interaction ω_{DD}^2 to the square of the frequency of TO lattice vibrations in diatomic cubic crystals can be expressed in terms of the mac-

roscopic parameters ε_∞ and Z, like the splitting between the LO and TO frequencies [see Eq. (3.55)].

The following expressions are obtained for the frequencies of LO and TO lattice vibrations[94]:

$$\omega_{TO}^2 = \omega_0^2 - \omega_{DD}^{\prime\prime}.$$

$$\omega_{LO}^2 = \omega_{TO}^2 + \frac{Z^2}{\varepsilon_\infty}\Omega^2 = \omega_0^2 + \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_\infty + 2}\right)Z^2\Omega^2$$

$$= \omega_0^2 + \frac{2}{\varepsilon_\infty}\omega_{DD}^2; \qquad (3.60)$$

here, ω_0^2 is the contribution of the short-range part of the direct Coulomb interaction representing the intracell interaction (overlap forces) and higher orders of the multipole expansion of the electron-nuclear and electron-electron interactions. The exact microscopic expression is obtained in Ref. 94 for ω_0^2. Equations (3.57)–(3.60) establish the relationship between the contribution of the dipole-dipole interaction to ω_{TO}^2 and ω_{LO}^2 with the macroscopic (transverse optical) Born charge Z or with the effective ion charge Z^i and with the electron permittivity ε_∞. There are exact analogs of the corresponding expressions obtained in the model of polarizable ions (see Sec. 2), but in contrast to the latter they do not contain ε_∞^{loc}, but the total electron permittivity ε_∞ and, moreover, in accordance with the microscopic derivation they are valid for compounds with an arbitrarily weak but finite ionicity. In the process of derivation the internal structure of the polarization operator $\hat{\pi}$ is ignored and, therefore, no approximations are made about the exchange-correlation interaction, whereas in the case of the electron spectrum it is simply assumed that there is a finite though arbitrarily small insulator gap.[94] It should also be mentioned that inclusion of higher terms of the multipole expansion and of the intracell interaction, i.e., of the difference between the actual microscopic field and the internal field, simply renormalizes the parameters of the dipole-dipole interaction without affecting the pole structure of the expressions in the system (3.57) associated with inclusion of the internal field. The effective ion charge Z^i appears in the theory precisely because of such renormalizations as a result of screening of the bare charge (nuclear charge) by the short-range part of the direct Coulomb interaction,[94] whereas in the model of polarizable ions the ion charge is a model parameter.

Lucovsky, Martin, and Burstein proposed earlier[34,35] (see also Ref. 21) to introduce into the theory not only the macroscopic Born charge Z, but also the localized effective charge Z^{loc} governing the contribution of the dipole forces (internal field) to ω_{TO}^2. An analysis of the meaning of the charge Z^{loc} made in Ref. 34 suggests that it is associated with localized excitation and that delocalized excitations of the charge density of the valence electrons make no contribution to ω_{DD}^2, so that the relationship between the dipole contribution to ω_{TO}^2 and the macroscopic parameters ε_∞ and Z is lost. In fact, the contribution of the dipole forces to ω_{TO}^2, i.e., ω_{DD}^2, is determined by the same macroscopic Born charge Z as the splitting between the LO and TO frequencies. This is a new and quite important feature of the description of lattice dynamics of polar crystals represented by Eq. (3.60).

It is clear from Eq. (3.60) for ω_{TO}^2 that softening of the frequency of TO vibrations or their instability may in general be due to a fairly large value of ω_{DD}^2 or the smallness of ω_0^2 (compared with normal crystals). It is naturally not possible to make any a priori conclusions on the nature of the

ferroelectric instability simply on the basis of Eq. (3.60). It is necessary to consider this problem either on the basis of microscopic calculations of the quantities ω_0^2 and ω_{DD}^2 or on the basis of an analysis of the experimental data for ε_∞, ω_{TO}, and ω_{LO} and subsequent comparison of ω_{TO}^2, ω_{DD}^2, and ω_0^2 in a series of isoelectronic compounds or for a group of compounds with a similar crystal structure. This will be done in the next section using compounds with NaCl and CsCl structures as an example.

We shall now consider in greater detail the band approach to the theory of ferroelectricity. It is in fact based on consideration of the band energy of the valence electrons

$$E_b = \sum_{\lambda,\,\mathbf{k}} n_{\lambda\mathbf{k}} E_{\lambda\mathbf{k}}, \tag{3.61}$$

where $n_{\lambda\mathbf{k}}$ and $E_{\lambda\mathbf{k}}$ are the occupation numbers and energies of single-particle Bloch states $|\lambda\,\mathbf{k}\rangle$. The usual reasoning is as follows.[98] A distortion of the lattice may increase (or give rise to) the insulator gap in the electron spectrum and can therefore reduce the band energy of the valence electrons. If the band energy reduction is greater than the increase in the elastic energy of the lattice, then in this approximation the initial structure is unstable and the lattice becomes modified. Essentially, in this approach the problem of the lattice stability is considered in the one-electron approximation. We shall show later that only a part of the change in the band energy capable of becoming unstable is considered.

The change in the band energy of Eq. (3.61) due to distortion of the lattice can be calculated using the Kohn-Sham equations [Eq. (3.19)]. With this in mind we shall represent V_{ext} in the form of an expansion in powers of displacements of the nuclei from equilibrium positions

$$V_{ext}(\mathbf{r}) = V_{ext}^{(0)}(\mathbf{r}) + \delta V_{ext}^{(1)}(\mathbf{r}) + \delta V_{ext}^{(2)}(\mathbf{r}) + \dots \ .$$

We can similarly describe the effective potential $V_{eff}(\mathbf{r})$ and the electron charge density $\rho_e(\mathbf{r}) = en(\mathbf{r})$. Next, solving Eq. (19) on the basis of perturbation theory, we can readily deduce a correction of the first order in respect of $\delta V_{eff}^{(1)}$, which should be applied to the wave function $\delta \varphi_i^{(1)}$ and of the second order in $\delta V_{eff}^{(1)}$ intended for the single-electron energy $\delta \widetilde{E}_i^{(2)}$. Consequently, the change in the band energy in the second order in $\delta V_{eff}^{(1)}$ is

$$\delta \widetilde{E}_b^{(r)} = \sum_i n_i \delta \widetilde{E}_i^{(2)} = \frac{e^2}{2} \sum_{i,\,j} |\langle j | \delta V_{eff}^{(1)} | i \rangle|^2 \frac{n_i - n_j}{E_i - E_j}$$

$$= \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}'\, \delta V_{eff}^{(1)}(\mathbf{r}) \pi^{(0)}(\mathbf{r}, \mathbf{r}') \delta V_{eff}^{(1)}(\mathbf{r}'), \tag{3.62}$$

and the change in the charge density of the valence electrons considered in the first order with respect to $\delta V_{eff}^{(1)}(\mathbf{r})$ is

$$\delta \rho_e^{(1)}(\mathbf{r}) = \pi^{(0)} \delta V_{eff}^{(1)} \equiv \int d\mathbf{r}\, \pi^{(0)}(\mathbf{r}, \mathbf{r}') \delta V_{eff}^{(1)}(\mathbf{r}'), \tag{3.63}$$

where

$$\pi^{(0)}(\mathbf{r}, \mathbf{r}') = e^2 \sum_{i,\,j}{}' \varphi_j(\mathbf{r}) \varphi_i^*(\mathbf{r}) \frac{n_i - n_j}{E_i - E_j} \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}') \tag{3.64}$$

is the polarization operator of noninteracting Bloch electrons. Using (3.18) for V_{eff}, and also Eq. (3.63) we can readily show that

$$\delta V_{eff}^{(1)} = \widetilde{\varepsilon}^{-1} \delta V_{ext}^{(1)}, \tag{3.65}$$

where the generalized permittivity matrix $\widetilde{\varepsilon}$ is governed by the following relationship[79]:

$$\widetilde{\varepsilon} = \hat{I} - \left(\hat{v}_c + \frac{\delta \hat{V}_{xx}}{\delta \rho_e}\right) \hat{\pi}^{(0)}. \tag{3.66}$$

Equation (3.62) readily yields the corresponding contribution to the force matrix and to the phonon spectrum of a crystal. It should be noted that the same result for the change in the phonon frequencies is obtained using the Fröhlich Hamiltonian

$$\hat{H} = \hat{H}_{ph} + \hat{H}_e + \hat{V}_{int}^{(1)},$$

$$\hat{H}_e = \sum_{\lambda\mathbf{k}} E_{\lambda\mathbf{k}} \hat{a}_{\lambda\mathbf{k}}^+ \hat{a}_{\lambda\mathbf{k}}, \tag{3.67}$$

$$\hat{H}_{ph} = \frac{1}{2} \sum_{\nu,\,\mathbf{q}} (\dot{Q}_{\nu\mathbf{q}}^* \dot{Q}_{\nu\mathbf{q}} + \bar{\omega}_\nu^2(\mathbf{q}) Q_{\nu\mathbf{q}}^* Q_{\nu\mathbf{q}}),$$

$$\hat{V}_{int}^{(1)} = \int d\mathbf{r}\, \hat{\Psi}^+(\mathbf{r}) (-e\delta V_{eff}^{(1)}(\mathbf{r})) \hat{\Psi}(\mathbf{r})$$

$$= \sum_{\substack{\lambda,\,\lambda',\,0 \\ \mathbf{k},\,\mathbf{q}}} g_{\lambda'\mathbf{k}+\mathbf{q},\,\lambda\mathbf{k}}^{(1)}(\nu) Q_{\nu\mathbf{q}} \hat{a}_{\lambda'\mathbf{k}+\mathbf{q}}^+ \hat{a}_{\lambda\mathbf{k}},$$

where

$$g_{\lambda'\mathbf{k}+\mathbf{q},\,\lambda\mathbf{k}}^{(1)}(\nu) = \frac{1}{N} \sum_s \frac{[e_s(\nu,\,\mathbf{q})}{M_s^{1/2}} \gamma_s(\lambda,\,\lambda';\,\mathbf{k},\,\mathbf{q}), \tag{3.68}$$

$$\gamma_s(\lambda,\,\lambda';\,\mathbf{k},\,\mathbf{q})$$

$$= e \int d\mathbf{r}\, \varphi_{\lambda'\mathbf{k}+\mathbf{q}}^*(\mathbf{r}) \varphi_{\lambda\mathbf{k}}(\mathbf{r})$$

$$\times \int d\mathbf{r}'\, \widetilde{\varepsilon}^{-1}(\mathbf{r},\,\mathbf{r}') \nabla' \sum_{\mathbf{R}} V_s(\mathbf{r}' - \mathbf{R} - \mathbf{R}_s) \exp[i\mathbf{q}(\mathbf{R} + \mathbf{R}_s)], \tag{3.69}$$

$\hat{a}_i^+$ and $\hat{a}_i$ are the electron creation and annihilation operators; $Q_{\nu\mathbf{q}}$, $e_s(\nu, \mathbf{q})$, and $\omega_\nu(\mathbf{q})$ are, respectively, the normal coordinates, polarization vectors, and bare phonon frequencies; V_s is the potential of the ion core of the sth sublattice. Renormalization of the phonon spectrum, i.e., the contribution of the valence electrons to the phonon spectrum in the model under consideration, is described by the familiar expression

$$\Delta \omega_\nu^2(\mathbf{q}) = \omega_\nu^2(\mathbf{q}) - \bar{\omega}_\nu^2(\mathbf{q})$$

$$= \sum_{\substack{\lambda,\,\lambda' \\ \mathbf{k}}}{}' |g_{\lambda'\mathbf{k}+\mathbf{q},\,\lambda\mathbf{k}}^{(1)}(\nu)|^2 \frac{n_{\lambda'\mathbf{k}+\mathbf{q}} - n_{\lambda\mathbf{k}}}{E_{\lambda'\mathbf{k}+\mathbf{q}} - E_{\lambda\mathbf{k}}}. \tag{3.70}$$

In many investigations of the "band" theory of ferroelectricity Eq. (3.70) is the starting point in dealing with the influence of the valence electrons on the stability of normal lattice vibrations at $T = 0$ K. Bearing in mind that since $(n_i - n_j)(E_i - E_j)^{-1} < 0$ and, consequently, $\Delta\omega_\nu^2(\mathbf{q}) < 0$, the instability of the lattice follows from Eq. (3.70) if the electron-phonon interaction is sufficiently strong. It should be stressed that the contribution to the phonon spectrum of the type described by Eq. (3.70), usually attributed to the renormalization of the phonon frequencies because of the electron-phonon interaction and partly to the effects associated with the nonadiabaticity of the electron subsystem,[40] does in fact appear also in the adiabatic approximation if we use Eq. (3.61) for the electron contribution to the total energy of the ground state [compare Eq. (3.70) with the expression (3.62) for $\delta \widetilde{E}_b^{(2)}$.] All the quantities occurring in Eq.

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(3.70) have exact microscopic meanings. The use of Eq. (3.70) and, consequently, of the Fröhlich Hamiltonian of Eq. (3.66) for the description of the contribution of the valence electrons to the phonon spectrum of a crystal and for the influence of these electrons on the stability of normal lattice vibrations must be qualified as follows. Firstly, Eq. (3.70) is far from the only contribution of the valence electrons to the phonon spectrum of a crystal and not even the only contribution when we consider simply the band energy of Eq. (3.61). Secondly (and this is more important), in many cases it is found, as shown later, that this contribution is not dominant at all in the appearance of the lattice instabilities.

First of all, an additional electron contribution associated with the band energy of Eq. (3.61) appears if we allow for $\delta V_{\text{eff}}^{(2)}$, which occurs even in the first order of the usual perturbation theory:

$$\delta \tilde{E}_b^{(2)} = -e \sum_i n_i \langle i \mid \delta V_{\text{eff}}^{(2)} \mid i \rangle = \int dr \, \rho_e^{(0)}(r) \, \delta V_{\text{eff}}^{(2)}(r). \quad (3.71)$$

The total electron contribution to lattice dynamics follows from variation of Eq. (3.19) for the total electron contribution to the ground-state energy in which the first term represents the band energy. Variation of the second, third, and fourth terms in Eq. (3.19) gives, with the aid of Eqs. (3.62) and (3.71), the following expression for the change in the total electron energy

$$\delta E_e^{(r)} = \frac{1}{2} \int dr\,dr' \; \delta V_{\text{eff}}^{(1)}(r)\, \pi^{(0)}(r, r')\, \delta V_{\text{eff}}^{(1)}(r')$$

$$- \frac{1}{2} \int dr\,dr' \; \delta\rho_e^{(1)}(r)\, v_c(r - r')\, \delta\rho_e^{(1)}(r')$$

$$- \frac{1}{2} \int dr\,dr' \; \delta\rho_e^{(1)}(r)\, \frac{\delta V_{xc}(r)}{\delta\rho_e(r')}\, \delta\rho_e^{(1)}(r')$$

$$+ \int dr\, \rho_e^{(0)}(r)\, \delta V_{\text{ext}}^{(2)}(r). \quad (3.72)$$

Therefore, in general the frequency of any normal vibration can be represented in the form

$$\omega^2(q) = \omega_{ii}^2 - \omega_1^2 - \omega_2^2 + \omega_{xc}^2 + \omega_3^2, \quad (3.73)$$

where ω_{ii}^2 is the contribution of the interaction between bare ion cores, $-\omega_1^2$, $-\omega_2^2$, and ω_3^2 are the contributions of the first, second, and fourth terms in Eq. (3.72), and ω_{xc}^2 is the exchange-correlation contribution corresponding to the third term in Eq. (3.72).

We shall now consider briefly the various contributions to Eq. (3.73). We note first of all that normal vibrations, unstable in a lattice composed of bare ion cores, are possible in a crystal, i.e., these vibrations are characterized by $\omega_{ii}^2 < 0$. The existence of such an instability for an arbitrary lattice is a trivial consequence of the Earnshaw theorem on the instability of classical systems held by the Coulomb forces; in crystals their stability is ensured by the electron contribution to the force matrix. The lattice-stabilizing contribution is ω_3^2, which is the last term in Eq. (3.72), contained also in Eq. (3.71). An example of normal vibrations unstable in a lattice of bare ion cores is given in Table I for the diamond-type structure. In principle, such a situation is possible in the case of normal vibrations corresponding to soft modes in ferroelectrics and antiferroelectrics. In this case the instability results from the smallness of the destabilizing electron con-

tribution to the force matrix, i.e., it is due to the weakness of the electron-phonon interaction. We shall limit ourselves to the case of normal vibrations which are stable in a lattice of bare ion cores ($\omega_{ii}^2 > 0$). Such a situation occurs, for example, in the case of long-wavelength TO lattice vibrations in cubic diatomic crystals [see Eq. (3.53)].

We shall be interested primarily in the quantity ω_1^2, which is the contribution of the first term to Eq. (3.71), frequently identified with the total contribution of the band energy, and assume this quantity to be responsible for the lattice instability in ferroelectrics.[37-40] The explicit expression for ω_1^2 is given by Eqs. (3.68)–(3.70). In the case under discussion ($\omega_{ii}^2 > 0$) the conclusion about the dominant role of ω_1^2 could not have raised any objections (and would have been trivial) if the remaining part of the electron contribution to $\omega^2(q)$ had been positive or known to be smaller than ω_1^2 in the absolute sense. In reality, neither is true. Among the other three terms only the contribution from the fourth term in Eq. (3.72) is known to be positive, whereas the sign and value of ω_{xc}^2 are difficult to determine without specific and detailed calculations and the contribution of the second term in Eq. (3.72) is negative, i.e., it can result in an instability when ω_2^2 is sufficiently large. This contribution describes the interaction of fluctuations of the charge density of the valence electrons and it should play an important role in those cases when the lattice distortion is accompanied by a modification of the charge density wave of the valence electrons, as is true, for example, in the case of a Peierls transition.

In view of the absence of sufficiently detailed calculations of ω_2^2 and ω_{xc}^2, we shall assume for the time being that they do not affect significantly the value of ω_{TO}^2 and we shall consider the more specific question of the relative values of ω_{ii}^2 and ω_1^2, i.e., we shall discuss whether the "band" contribution can of itself result in the lattice instability. One of the possible ways of estimating ω_1^2 is to calculate it using some model of the energy band structure. The fullest calculations of this kind have been made in connection with the stability of lattice vibrations in cubic diatomic crystals. The Penn model[100] of the band structure of semiconductors is used in Ref. 99 to find the following expressions for the macroscopic charge Z and for the "band" contribution to ω_{TO}^2

$$\varepsilon_\infty = 1 + \frac{4\pi e^2 N_v}{m v_0 E_{av}^2}, \qquad Z = \frac{1}{2}(Z_c - Z_a) + \delta Z_e,$$

$$\delta Z_e = \frac{3N_v}{k_F} \frac{|\Xi|}{E_{av}}, \qquad \omega_1^2 = \frac{3N_v}{\mu} \frac{|\Xi|^2}{2E_F}; \quad (3.74)$$

here, E_F and k_F are the Fermi energy and momentum of the valence electrons in the Penn model ($k_F^2 = 3\pi^2 N_v / v_0$); N_v is the number of valence electrons per unit cell; E_{av} is the insulator gap on the Fermi surface (average band gap)[100]; Ξ is the deformation potential averaged over the Fermi surface; $Z_c e$ and $Z_a e$ are the charges of ion cores of the cation and anion, respectively. If we express Ξ and E_{av} in terms of δZ_e and ε_∞, we find that[99]

$$\omega_1^2 = \frac{4\pi e^2}{3\mu v_0} \frac{\delta Z_e^2}{\varepsilon_\infty - 1}, \qquad \delta Z_e = Z + \frac{Z_a - Z_c}{2}, \quad (3.75)$$

and hence, using Eq. (3.70), we obtain

$$\omega_{ii}^2 - \omega_1^2 = \frac{4\pi e^2}{3\mu v_0} \left(Z_c Z_a - \frac{\delta Z_e^2}{\varepsilon_\infty - 1} \right). \quad (3.76)$$

Equations (3.75) and (3.76) contain only the experimental values and the charges of stripped ion cores, so that we can estimate ω_1^2 and compare it with ω_{ii}^2. The experimental data for Z and ε_∞ of some diatomic cubic crystals will be given in the next section. In the case of IV–VI compounds close to the unstable state the second term inside the parentheses of Eq. (3.76) does not exceed 2, whereas $Z_c Z_a = 24$. Therefore, it follows from the above estimates that the "band" contribution to ω_{TO}^2 described by Eqs. (3.62) or (3.70) is in the case of diatomic cubic semiconductors at least an order of magnitude less than the contribution of bare ion cores ω_{ii}^2 and cannot be responsible for the instability of TO lattice vibrations in the cubic phase of IV–VI compounds.

However, as stressed in Ref. 101, in the case of IV–VI compounds in the cubic phase the band gap on the surface of a Jones zone, which is the Fermi surface in the extended **k** space, is strongly anisotropic and the Penn model is a poor approximation for the description of the energy band structure of these compounds. An analytic model of this band structure, which describes the features of the origin of the electron spectrum of IV–VI compounds, was developed on the basis of the LCAO method[102] in Refs. 103 and 104. Within the framework of this model using the nearest-neighbor approximation, i.e., in fact for a linear diatomic chain of atoms A and B, expressions have been found for ε_∞ (Ref. 93), for the macroscopic charge Z (Ref. 105), for the "band" contribution to ω_{TO}^2, i.e., for ω_1^2 (Refs. 103 and 105):

$$\varepsilon_\infty = 1 + \frac{4}{3} \frac{e_2}{a_0} \cdot \frac{\xi_0}{\Delta_{ion}^2} , \qquad Z = \delta Z_e - 1,$$

$$\delta Z_e = \frac{2}{\pi} \frac{Ia_0}{\Delta_{ion}} , \qquad \omega_1^2 = \frac{2}{\pi} \frac{I^2}{\mu \xi_0} \ln \frac{\xi_0}{\Delta_{ion}} ; \tag{3.77}$$

where I is the deformation potential; $2\Delta_{ion}$ is the gap in the electron spectrum obtained on allowance for the density of states in IV–VI compounds; ξ_0 is the width of the valence band. The logarithmic dependence of ω_1^2 on Δ_{ion} is a consequence of the quasi-onedimensional nature of the model. Using an estimate $\Delta_{ion}/\xi_0 \sim 0.3$ obtained for PbTe in Ref. 105, we find that the logarithmic factor can be omitted. Consequently, expressing I and Δ_{ion} in terms of ε and Z_e, we find again—as in the Penn model—Eq. (3.75) for ω_1. Therefore, in two limiting cases—the isotropic approximation of almost-free electrons of Eq. (3.74) and the strongly anisotropic tight-binding approximation of Eq. (3.77)—we obtain the same expression (3.75) for ω_1^2 in terms of the macroscopic parameters ε_∞ and Z, which justifies the use of this expression for the above estimate of ω_1^2 obtained for IV–VI compounds.

The expression (3.75) for ω_1^2, like the expressions (3.74) and (3.77) for ε_∞ and Z represent—bearing in mind their derivation—the interband contribution to these quantities made by regions with a high density of states.[100,103] In the case of narrow-gap semiconductors, which include IV–VI compounds, a considerable contribution can be made generally by regions with a low density of states near the band edges (in the vicinity of the points L of the Brillouin zone in the cubic phase of IV–VI compounds).[38–40] However, estimates obtained for ω_1^2 in Ref. 106 demonstrate that the contribution of the points L to ω_1^2 is within the range 100–5500 cm^{-2}, i.e., it is small compared with the contribution of stripped ion cores $\omega_{ii}^2 \sim 10^5$ cm^{-2}, so that the former

cannot have a significant influence on the stability of TO lattice vibrations in the cubic phase of IV–VI compounds.

We have ignored so far the stabilizing electron contribution to ω_{TO}^2, i.e., the contribution of the fourth term in Eq. (3.72). As shown above, this contribution gives rise to a characteristic structure of the electron contribution to the force matrix [see Eqs. (3.23), (3.26), and (3.32)] guaranteeing the translational invariance of the total energy of the system and the existence of acoustic vibrations. This means, in particular, that if in any approximation we find the contribution of $\delta V_{ei}^{(1)}$ to the force matrix [we shall denote it by $c_{si,lj}$ (**q**)], then the contribution of $\delta V_{ei}^{(2)}$, i.e., of the fourth term in Eq. (3.72), contains in the same approximation the contribution to the force matrix of the type

$$-\delta_{st} \sum_u C_{si, uj} (0)$$

and the contribution to the phonon spectrum then becomes

$$\Delta \omega_\nu^2 (\mathbf{q}) = \sum_{s,t} \frac{e_{si}(\nu, \mathbf{q})}{M_s^{1/2}} C_{si, lj} (\mathbf{q}) \frac{e_{tj}(\nu, \mathbf{q})}{M_t^{1/2}}$$
$$- \sum_{s,t} \frac{e_{si}^*(\nu, \mathbf{q}) e_{sj}(\nu, \mathbf{q})}{M_s} C_{si, tj}(0).$$

In the "band" approximation [see Eqs. (3.68)–(3.70)] the total contribution of the band energy to ω_{TO}^2 in the case of diatomic cubic crystals is described by $[e_s(TO) = (-1)^2 (\mu/M_s)e_\perp]$

$$\tilde{\omega}_{TO}^2 = \omega_{ii}^2 - \frac{1}{\mu N} \sum_{\substack{\lambda, \lambda' \\ \mathbf{k}}}{}' [(\gamma_1 (\lambda, \lambda'; \mathbf{k}) e_\perp)^* (\gamma_2 (\lambda, \lambda''; \mathbf{k}) e_\perp)$$
$$+ (\gamma_2 (\lambda, \lambda'; \mathbf{k}) e_\perp)^* (\gamma_1 (\lambda, \lambda'; \mathbf{k}) e_\perp)] \frac{n_{\lambda'\mathbf{k}} - n_{\lambda\mathbf{k}}}{E_{\lambda'\mathbf{k}} - E_{\lambda\mathbf{k}}} .$$

Noting that

$$- [(\gamma_1 e_1)^* (\gamma_2 e_\perp) + (\gamma_1 e_\perp)^* (\gamma_1 e_\perp)]$$

$$\equiv \sum_s | (\gamma_s e_\perp) |^2 - | \sum_s (\gamma_s e_\perp) |^2,$$

we find that inclusion of the non-Fröhlich terms of the second order in displacements of nuclei when considering the electron-phonon interaction generally results in the loss of the variable-sign band contribution to ω_{TO}^2.

One should make further comment at this point on the role of the various terms in Eq. (3.73) in the case of the Peierls instability of a crystal, which occurs in quasi-one-dimensional metals or metals and semimetals with nesting parts of the Fermi surface.[98] It is the Peierls instability in a cubic metallic precursor phase which is assumed to be responsible for the observed crystal and electron structure of group V elements (belonging to the bismuth group).[107] In the Peierls situation the polarization operator is known to diverge at a wave vector **Q** joining the nesting parts of the Fermi surface: $\pi^{(0)}(\mathbf{q} \to \mathbf{Q}) \to \infty$. Consequently, the electron permittivity ε_∞ ($\mathbf{q} \to \mathbf{Q}$) diverges. Using Eqs. (3.65) and (3.67)–(3.70), we can see that the "band" contribution due to the screening by the electron potential generally vanishes in the Peierls case making no contribution to the frequency of the corresponding normal mode. In this case the presence or absence of a real instability of a crystal is governed entirely by the relationship between the ion-ion contribution ω_{ii}^2

and the contribution of the direct Coulomb interaction of fluctuations of the charge density of the valence electrons ($-\omega_2^2$), and also by the quantity ω_{xc}^2. A more detailed discussion of this problem can be found in a paper by one of the present authors.[43]

4. FERROELECTRIC PROPERTIES OF IV-VI COMPOUNDS

In diatomic compounds with the NaCl or CsCl structure the transition from wide-gap insulators with a low electron polarizability to semiconductors reveals a tendency for the manifestation of the properties typical of virtual displacive ferroelectrics: the frequencies of long-wavelength TO lattice vibrations ω_{TO} become softer, the low-frequency permittivity ε_0 rises at low temperatures, and the sign of the temperature coefficients of ω_{TO} and ε_0 is reversed (Table III). Such ferroelectric properties are manifested most clearly by five IV-VI compounds with anomalously high values of ε_∞ in the cubic phase[108] (Table III). This tendency is exhibited among IV-VI compounds themselves; as we go from PbS to GeTe crystals the increase in ε is accompanied by a reduction in the stability of the cubic phase at low temperatures. In the case of lead chalcogenides the cubic phase is stable right up to $T = 0$ K (Ref. 112), but there is a considerable softening of ω_{TO} and ε_0 has anomalously large values, SnTe is a virtual or low-temperature ferroelectric with $T_c \lesssim 150$ K (Refs. 113–115), whereas GeTe is a high-temperature ferroelectric with $T_c = 630$–700 K (Refs. 112 and 116). The temperature of the phase transition T_c in these compounds is a function of the concentration of nonstoichiometric defects (tin or germanium vacancies) and it decreases on increase in the vacancy concentration.[6] More detailed reviews of the experimental results obtained for IV–VI compounds can be found in Refs. 112, 119, and 120.

In the classical microscopic theory the ferroelectric properties can be explained by the dipole instability of TO lattice vibrations. In the case of polyatomic ferroelectrics, such as those with the perovskite structure, the dipole contribution is large because of the anomalously large internal field constants. In the case of diatomic crystals the internal field is Lorentzian and the dominant role is played by characteristics of the electron structure, when the classical theory of ionic crystals cannot be used in the case of IV–VI com-

pounds. In the preceding sections we derived general expressions for the contribution of the dipole forces in diatomic cubic crystals which make it possible to account for the role of these forces in the establishment of ferroelectric properties of IV–VI compounds and to relate these properties to the characteristics of the electron structure.[121] It follows from Eq. (3.58)–(3.60) that when the dipole contribution is sufficiently large, it may result in instability of TO vibrations. We can also see that this is favored by high values of ε_∞. On the other hand, as pointed out already, instabilities are also favored by low values of ω_0^2. Therefore, although ε_∞ of IV–VI compounds is anomalously large, because of the low ionicity of these compounds the effective ion charge Z^i should be small and it is not a priori clear that this will result in an instability.

The possibility of the nondipole mechanism of the lattice instability in IV–VI compounds is suggested by some characteristics of the electron structure and chemical binding of these compounds. The ionicity of IV–VI compounds is low so that their electron properties are closer to those of nonpolar group V semimetals with metallic cubic phases than to ionic insulators. Therefore, the problem of stability of the cubic phase of IV–VI compounds was discussed in Refs. 103, 122, and 123 by analogy with group V semimetals which have crystal structures than can be derived by a slight distortion of the simple cubic lattice, the distortion being a shift of the sublattices along a threefold axis and a rhombohedral deformation of the kind encountered in the ferroelectric phases of SnTe and GeTe. It was shown there that the ionicity[7] stabilizes only the cubic phase of IV–VI compounds which at first sight seems to be in direct conflict with the idea of the dipole mechanism of the ferroelectric instability of these compounds, because optical lattice vibrations in diatomic crystals become dipole-active only if the compounds are ionic.

A detailed analysis of the influence of the dipole forces on the stability of TO vibrations in the cubic phase of IV–VI compounds was made in Ref. 121. We can see from Eqs. (3.59) and (3.60) that the dipole contribution to ω_{TO}^2 can be expressed in terms of the same macroscopic parameters ε_∞ and Z as the splitting between the LO and TO frequencies. This makes it possible to find the values of ω_0^2 and ω_{DD}^2 using the experimental data on ε_∞, ω_{LO}, and ω_{TO}, i.e., without

TABLE III. Experimental values of the difference between the ionization potentials $I_B - I_A$ of B and A atoms in a compound AB, of the electron permittivity ε_∞, and of the frequencies of TO and LO lattice vibrations. The citations of the papers from which the results were taken can be found in Ref. 121. The values of the parameter γ were obtained using the Lyddane-Sachs-Teller relationship [see Eq. (3.56)]. The frequency Ω is defined by Eq. (3.53). The data for SnTe correspond to the composition $Sn_{0.984}Te$ with the hole density $p = 5\times10^{20}$ cm^{-3} [$p_H(77$ K$) = 8\times10^{20}$ cm^{-3}]. In the case of GeTe the difference between the ionization was $I_B - I_A = 1.13$ eV.

| Compound	Type of lattice	$I_B - I_A$, eV	$\gamma = \frac{\varepsilon_0}{\varepsilon_\infty}$		ε_∞		ω_{TO}^2 cm^{-2}		ω_{LO} cm^{-1}		Ω, cm^{-1}
		eV	4 K	300 K	4 K	300 K	4 K	300 K	4 K	300 K	
1. NaCl	NaCl	7,87	2,3	2,5	2,35	2,33	178	164	272	261	281
2. CsCl	CsCl	9,12	2,5	2,6	2,67	2,63	106	100	168	162	159
3. TlCl	do.	6,90	8,4	7,8	5,0	4,76	60,5	62,0	175	173	171
4. TlBr	do.	5,73	6,8	6,1	5,64	5,34	45,0	47,0	117	116	117
5. PbS	do.	2,94	—	10	17	17	—	67	212	212	184
6. PbSe	do.	2,34	13,6	13,6	24	22	39	39	144	144	122
7. PbTe	do.	1,60	40	12,6	36	32	18	32	114	114	95
8. SnTe	do. do.	1,67	90	10	40±2	37±2	15	44,5	140	140	113
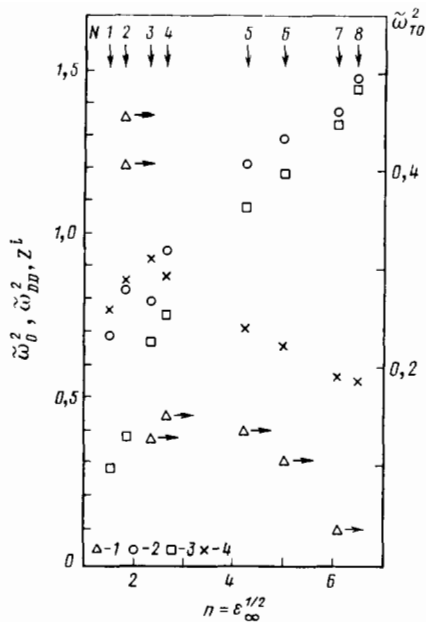
FIG. 1. Values of $\tilde{\omega}_{TO}^2$, $\tilde{\omega}_0^2$, $\tilde{\omega}_{DD}^2$, and Z^i (Ref. 121). See Eq. (4.1) and the explanations in text. The vertical arrows identify the number of a compound in Table III. Meaning of symbols: 1) $\tilde{\omega}_{TO}^2$; 2) $\tilde{\omega}_0^2$; 3) $\tilde{\omega}_{DD}^2$; Z^i

recourse to any model calculations. If we allow for Eq. (3.59), this applies also to the parameter Z^i. Since diatomic cubic crystals have been investigated thoroughly in the experimental sense, we can use Eqs. (3.58)–(3.60) to analyze the influence of the dipole forces on the stability of TO lattice vibrations in IV–VI and other diatomic cubic crystals. A measure of proximity of a cubic phase to an unstable state can be provided by the values of ω_{TO}^2 measured in units of Ω^2 [see Eq. (3.71)], i.e., by the dimensionless force constant

$$\tilde{\omega}_{TO}^2 = \tilde{\omega}_0^2 - \tilde{\omega}_{DD}^2, \quad \tilde{\omega}_0^2 = \frac{\omega_0^2}{\Omega^2},$$

$$\tilde{\omega}_{DD}^2 = \frac{Z^2}{\varepsilon_\infty + 2} = \left(\frac{Z^i}{3}\right)^2 (\varepsilon_\infty + 2), \quad (4.1)$$

which makes it possible to compare these quantities for different compounds. Figure 1 shows the values of $\tilde{\omega}_{TO}^2$, $\tilde{\omega}_0^2$, $\tilde{\omega}_{DD}^2$, and Z^i for two groups of ionic crystals with the NaCl and CsCl structures and for lead chalcogenides and also for SnTe (specifically for the composition which is a virtual ferroelectric with $T_c < 0$), found from the low-temperature data for ε_∞, ω_{LO}, and ω_{TO}. It is clear from Fig. 1 that the reduction in ω_{TO}^2, i.e., the reduction in the stability of TO lattice vibrations, is accompanied by an increase in $\tilde{\omega}_0^2$ and $\tilde{\omega}_{DD}^2$ on transition from one group of compounds to the other, as well as within the series of IV–VI compounds themselves. Therefore, the reduction in ω_{TO}^2 is entirely due to an increase of the contribution of the dipole forces to ω_{TO}^2, since the contribution of all other interactions included in ω_0^2 tends to stabilize TO vibrations as demonstrated by the dipole mechanism of the instability of the cubic phase of IV–VI compounds.

The reduction in the stability of TO vibrations is accompanied by a reduction of the effective ion charge Z^i, in agreement with the observed reduction in the ionicity in the investigated series of compounds. Therefore, as can be seen from Eq. (3.58), the increase in $\tilde{\omega}_{DD}^2$ and the reduction in the

stability of TO vibrations in diatomic cubic crystals with the NaCl or CsCl structure is related mainly to the increase in ε_∞, whereas in IV–VI compounds it is entirely due to the increase in ε_∞. We can see from Fig. 1 and Table III that the extrapolation of the dependence $\tilde{\omega}_{TO}^2$ on ε_∞ predicts a change in the sign of ω_{TO}^2, i.e., it predicts an instability of TO vibrations in the range $\varepsilon_\infty \gtrsim 45$, which is in good agreement with the observed dependences of ε_∞ (Ref. 110) and T_c (Ref. 114) on the composition of $Sn_{1-x}Te$.

The results obtained allow us to draw the conclusion that the stability of TO lattice vibrations at low temperatures in the cubic phase of SnTe and GeTe and the proximity to the unstable state of lead chalcogenides are all consequences of anomalous dielectric properties of the electron subsystem of IV–VI compounds. This result allows us to link the dipole mechanism of the ferroelectric instability of IV–VI compounds with the origin of the electron spectrum of the cubic phase of these compounds[103,104,101,123] and with the approach to the problem of the structural instability of the cubic phase of IV–VI compounds based on the proximity of electron properties of these compounds to those of nonpolar bismuth-group semimetals.

The electron structure of the cubic phases of IV–VI compounds is discussed using the LCAO method in Refs. 103 and 104 and the pseudopotential method in Refs. 123 and 101, and its origin is attributed to the structure of a metallic precursor phase, which is obtained if we ignore the chemical inequivalence of atoms in the two sublattices A and B and which is an analog of the cubic phase of bismuth. The ionicity and the insulator gap in the electron spectrum of the cubic phases of IV–VI compounds appear due to the potential V_a of the valence electrons, which is antisymmetric relative to the operations causing transposition of sublattices in the NaCl structure, provided an allowance is made for the chemical inequivalence of the B and A atoms. It is important to note that this not only produces the minimum gap E_g located in the case of IV–VI compounds in the vicinity of the points L of the Brillouin zone, but also the average gap E_{av} corresponding to the position of the principal maximum Im $\varepsilon(\omega)$ and governing the value of ε_∞ in the case of IV–VI compounds.

The nature of the anomalous rise of ε_∞ in the IV–VI series can be understood if we consider the metallic precursor phase as a special case of the semiconductor phase in the limit $V_a \to 0$ bearing in mind that in the first approximation the series of compounds PbS, PbSe, PbTe, SnTe, and GeTe can be regarded as states of the semiconductor phase in the decreasing order of V_a (Refs. 103, 104, 122, and 123). Metallization of the electron spectrum of the cubic phases of IV–VI compounds on transition from PbS to GeTe is manifested by a reduction in the average band gap E_{av} between the filled and empty states[124] and is accompanied by an anomalous increase in ε_∞ (Refs. 93 and 125).

We can therefore say that considerable softening of ω_{TO} exhibited by lead chalcogenides and the ferroelectric instability of SnTe and GeTe are all consequences of the proximity of the cubic phase of these compounds to the metallic state associated with the smallness of V_a: as V_a is increased, the permittivity ε_∞ rises and this in turn increases the contribution of the dipole forces to ω_{TO}^2, resulting in an instability of TO lattice vibrations. If we bear in mind that the potential

V_a determines the degree of ionicity, this means that the reduction in the ionicity along the IV–VI series favors an increase in the contribution of the dipole forces to ω_{TO}^2, i.e., it reduces the stability of TO vibrations. It is clear from Eq. (3.58) that this is associated with the structure of ω_{DD}^2: the fall of the effective charge Z^i due to the reduction in the ionicity is compensated by a simultaneous rise of ε_∞. Obviously, these results are in full agreement with the conclusions reached in Refs. 103, 122, and 123 that an increase in the ionicity stabilizes the cubic phases of IV–VI compounds. It should also be noted that the term "effective ion charge" for the parameter Z^i is used by analogy with the model of polarizable ions and that the relationship between Z^i and the ionicity is purely empirical (Fig. 1), but does not follow directly from the microscopic expression for Z^i obtained in Ref. 94. We can reveal this relationship using the exact expression (3.58) and theory of Refs. 93 and 105 relating ε_∞ and Z to the ionicity Δ_{ion}. The necessary expressions are given by Eq. (3.77). Using them and Eq. (3.72), we find that

$$Z^i = \frac{3Z}{\varepsilon_\infty + 2} \approx \frac{9}{2\pi} \frac{Ia_0^2}{e^2} \frac{\Delta_{ion}}{\xi_0}. \tag{4.2}$$

It is clear from Eq. (4.2) that we have $Z^i \to 0$ in the limit $V_a \to 0$ and, consequently, Z^i can be regarded as a measure of the ionicity of IV–VI compounds. Using parameters typical of IV–VI compounds ($Ia_0 \sim 10$ eV, $\xi_0 \sim 3$–5 eV, $\Delta_{ion} \sim 0.5$–1 eV),[93] we find from Eq. (4.2) that $Z^i \sim 0.3$–1, which is in good agreement with the values of Z^i reported for IV–VI compounds.

In the above discussion we relied heavily on the fact that the average band gap E_{av} governing the value of ε_∞ is purely of ion origin in the cubic phases of IV–VI compounds.[8] In fact, all this applies also to III–V and II–VI semiconductor compounds with the sphalerite structure with one, but important, difference: the precursor phase for the latter compounds has the diamond structure and the covalent binding. The values of E_{av} for III–V and II–VI compounds include not only an ionic contribution, but also a covalent contribution E_{av}^{cov} (Refs. 126–128) and on reduction in the ionicity ($V_a \to 0$) we find that $Z^i \to 0$, but ε_∞ tends to a finite value governed by E_{av}^{cov} so that $\tilde{\omega}_{DD}^2$ tends to zero when $V_a \to 0$. Consequently, in spite of an increase in ε_∞ the transition from IV–VI to III–V compounds reduces the dipole contribution made to $\tilde{\omega}_{TO}^2$ of III–V compounds compared with II–VI compounds (by a factor of 1.5–2) and by a much larger factor (3–5) compared with IV–VI compounds. Clearly, the covalence is also responsible for the anomalously large values of $\tilde{\omega}_0^2$ reported for these compounds (1.5–2 times greater than for IV–VI compounds). This is supported, in particular, by the rise of $\tilde{\omega}_0^2$ on transition from II–VI compounds to IV elements. Although metallization of the electron spectrum increases also $\tilde{\omega}_0^2$ (Fig. 1), if the dipole forces are allowed for, the influence of metallization and covalence on the stability of TO vibrations in diatomic cubic crystals is very different. The covalence suppresses the dipole forces and stabilizes only TO vibrations, whereas metallization of the chemical binding increases $\tilde{\omega}_{DD}^2$ and tends to make TO vibrations unstable. The consequence is the different influence of the ionicity on the stability of TO vibrations in crystals with ionic-metallic and ionic-covalent types of chemical binding: in the former the ionicity stabilizes TO vibrations, whereas in the latter the ionicity destabilizes these vibrations.

We mentioned earlier an approach to the problem of stability of the cubic phases of IV–VI compounds based on a similarity of the electron properties of these compounds with those of group V semimetals.[103,122,123] This approach was developed most thoroughly by Volkov and Pankratov[103] on the basis of an analytic model of the band structure of IV–VI compounds which they proposed and which we discussed already. This approach is based on the following reasoning. The p valence electrons form, if we ignore the weak hybridization effects and the spin-orbit interaction, systems of three mutually perpendicular one-dimensional half-filled energy bands in the precursor phase, so that this metallic phase exhibits the Peierls instability as a result of a mutual shift of two sublattices along the [111] axis in the NaCl structure, as exhibited by Bi, Sb, and As. An additional allowance for the ionicity and possibly for the spin-orbit interaction may stabilize the cubic structure of IV–VI compounds, which accounts for the stability of the NaCl structure in the case of lead chalcogenides.

A different approach to the problem of stability of TO lattice vibrations in diatomic cubic crystals and particularly in IV–VI compounds was proposed by Porod and Vogl.[36] Their "analytic model" is based[36] on the diagonal approximation for the $\tilde{\chi}(\mathbf{K}, \mathbf{K}')$ matrix in Eq. (3.54), i.e., it is based on an allowance for just the diagonal components of $\pi(\mathbf{K}, \mathbf{K}')$ characterized by $\mathbf{K}' = \mathbf{K}$ in Eq. (3.51) for $\tilde{\chi}$. We shall not repeat the demonstration given in Ref. 36 of the considerable influence of the contribution of the diagonal components of π to ω_e^2 on the stability of TO vibrations in diatomic cubic crystals: the treatment is sufficiently full in Ref. 36, but it should be mentioned that the arguments given there are not supported by numerical calculations of ω_{TO}^2 or of contributions of the off-diagonal components of π to ω_e^2, made in Refs. 36 and 87 (see Table II). We can see from this table that the "analytic model" gives rise to large values of ω_{TO}^2 for the cubic phases of IV–VI compounds and these values do not agree even in respect of the order of magnitude with the experimental data on ω_{TO}^2 and, moreover, the model does not reflect the tendency for the reduction in the stability of TO vibrations along the PbS, ... , GeTe series. Moreover, we have doubts about the conclusion[36] that the off-diagonal components of $\pi(\mathbf{K}, \mathbf{K}')$ are small for IV–VI compounds and about the consequent conclusion that the contribution of these components to ω_{TO}^2 is unimportant, because we can see from Table II that the contribution is large and it results in a strong instability of TO vibrations of IV–VI compounds. It should also be noted that in order to calculate the off-diagonal components of $\hat{\pi}$ we cannot use the jellium model of Ref. 36 and we have to allow for the insulator gap on the Fermi surface of the valence electrons (on the surface of the Jones zone), i.e., we have to allow for E . Therefore, the conclusion reached in Ref. 36 that there is no relationship between ε_∞ and the stability of TO lattice vibrations in IV–VI compounds, which is based on an analysis of $\tilde{\chi}(\mathbf{K}, \mathbf{K}')$ in the jellium model, is not convincing and moreover it is in conflict with the experimental results.

We have discussed here only the problem of the stability of TO lattice vibrations in the cubic phase at $T = 0$ K restricting ourselves to the harmonic approximation in the description of lattice dynamics. When other topics are consid-

ered, for example, the temperature dependences of ε_0, ω_{TO}, and ω_{LO} in the cubic phases of IV–VI compounds and the structure of the low-temperature phases of SnTe and GeTe, we need to include the anharmonicity of lattice vibrations. In particular the temperature dependence of ω_{TO} for the cubic phase is given by the expression[9]

$$\omega_{TO}^2(T) = \omega_{TO}^4(0) + \Sigma_{TO}(T), \quad \Sigma(T) \equiv \Sigma(i\omega_n = 0), \quad (4.3)$$

where $\Sigma_{TO}(T)$ is the self-energy part allowing for the phonon-phonon interaction associated with the lattice anharmonicity. In the case of weakly anharmonic crystals a theory based on the lattice Hamiltonian of Eq. (3.38) predicts two contributions to Σ: of the first order in $\hat{V}_4$ and of the second order in $\hat{V}_3$ (Ref. 5):

$$\Sigma = \Sigma^{(4)} + \Sigma^{(3)} = \qquad\qquad + \qquad\qquad , \quad (4.4)$$

where the wavy line is the temperature (Matsubara) phonon Green function. There is also a contribution of thermal deformation, but it is usually small. Since $\Sigma^{(4)} > 0$ and $\Sigma^{(3)} > 0$, the sign of $\Sigma(T)$ depends on the relationship between these two contributions. It is usually stressed that $\Sigma(T)$ for displacive ferroelectrics is of the same order of magnitude as for normal (nonferroelectric) insulators.[5,6] However, it is important to stress that whereas in the case of normal insulators we have $\Sigma(T) < 0$, i.e., the frequency of TO vibrations becomes softer on increase in temperature (Table III), in the case of real ferroelectrics with $\omega_{TO}^2(0) = -\omega_c^2 < 0$ we can expect stabilization of TO vibrations above T_c if $\Sigma_{TO}(T) > 0$. The change in the behavior of $\Sigma_{TO}(T)$ is smooth (Table III) as $\omega_{TO}^2(0)$ becomes softer. This matched behavior of $\Sigma_{TO}(T)$ and of the harmonic approximation frequencies is clearly not accidental, but it cannot be explained by the phenomenological theory of the lattice anharmonicity.[5,6]

An "electron" mechanism of stabilization of TO vibrations within the framework of the "band" approach was proposed in Ref. 39: the authors used the Hamiltonian of Eqs. (3.82)–(3.84) to allow for contributions of the fourth order in V_{int} to $\Delta\omega_{TO}^2$, giving rise to the following temperature dependence of ω_{TO}^2:

$$\Delta\omega_{TO}^2 = c \qquad\qquad c + c \qquad\qquad c$$
$$+ c \qquad\qquad c + c \qquad\qquad , \quad (4.5)$$

where the bare electron loop represents Eq. (3.65) and the last three graphs describe the electron contribution to $\Sigma(T)$. If $T \gtrsim \theta_D$, then $\Sigma_e(T) = AT$, where $A > 0$. It is stressed in Ref. 39 that inclusion of $\Sigma_e(T)$ makes it unnecessary to consider the lattice anharmonicity. However, firstly, as is clear from the discussion at the end of Sec. 2a, there is no "electron" anharmonicity apart from that which is obtained by expanding the adiabatic potential and one can speak only of a calculation of the electron contribution to the lattice anharmonicity. We can easily see that the last three graphs in Eq. (4.5) describe the simplest electron contribution to $\Sigma^{(4)}(T)$ of Eq. (4.4), which appears because of the next electron contribution to the four-phonon interaction

$$\qquad\qquad \equiv \qquad\qquad . \quad (4.6)$$

Secondly, on the basis of the model described by Eqs. (3.68)–(3.70), if we add acoustic phonons, we can write down directly the corresponding contribution to $\Sigma^{(3)}(T)$:

$$\Sigma_e^{(3)}(T) = c \qquad\qquad c , \qquad \equiv \qquad . \quad (4.7)$$

where a and c are the acoustic and critical phonons, and the designations 1 and 2 for the electron lines in Eqs. (4.6) and (4.7) correspond to different (valence or conduction) bands. If $T \gtrsim \theta_D$, then $\Sigma_e^{(3)} = -BT$, where $B > 0$. Consequently, without any specific calculations of the constants A and B we cannot determine the sign of $\Sigma(T)$ even on the basis of the "band" model.

The total electron contribution to $\Sigma_{TO}(T)$ can be represented as a series in powers of terms in the expansion of the electron-nuclear ($\hat{V}_{ne}^{(1)}$, $\hat{V}_{ne}^{(2)}$, $\hat{V}_{ne}^{(3)}$, $\hat{V}_{ne}^{(4)}$, etc.) or the electron-ion interactions and if we include the electron-electron Coulomb interaction, we find that the structure is very complex. We can however show that if we consider $\mu\omega_{TO}^2$ as elastic constants of the corresponding long-wavelength optical displacements, then Eqs. (3.58)–(3.60) for the contribution of the dipole forces to ω_{TO}^2 and ω_{LO}^2 retain their form in all orders of the anharmonicity and are valid at finite temperatures if ε_∞, Z, Z', and ω_0^2 are replaced with the corresponding temperature-dependent quantities. This makes it possible to use Eqs. (3.59)–(3.60) for the analysis of the temperature dependences of ε_∞, ω_{TO}, ω_{LO}, and ε_0 for the cubic phases of IV–VI compounds.[121] The analysis reported in Ref. 121 shows that at high temperatures the stabilization of TO lattice vibrations in the cubic phase of IV–VI compounds is entirely due to a reduction in ε_∞ on increase in temperature. It is unusual to note that the stabilization becomes more effective the stronger the instability at $T = 0$ K: the rate of fall of ε_∞ in the cubic phases of IV–VI compounds on increase in temperature rises on increase in ε_∞ ($T = 0$ K). This can be explained by the pole structure of the expressions in Eq. (3.57) for ε_∞ and ω_{DD}^2 associated with inclusion of the internal field. On the other hand, the dipole contribution to ω_{LO}^2 in the case of IV–VI compounds depends weakly on ε_∞ and is small, which makes it possible to explain the observed absence of the temperature dependence of ω_{LO} in the cubic phases of IV–VI compounds. The nature of the temperature dependences[10] of the permittivity ε_∞ and of ω_{TO}^2 for the cubic phases of IV–VI compounds, due to the pole structure of the contribution of the internal field to ε_∞ and ω_{DD}^2, is confirmed by the available experimental data for these compounds (Fig. 2).[11]

We can therefore say that the dipole forces in IV–VI compounds are responsible both for the instability of TO vibrations in the cubic phases at low temperatures if the values of ε_∞ (0 K) are sufficiently high and also for the stabilization of TO vibrations at high temperatures due to the fact that the increase in ε_∞ (0 K) is accompanied by an increase (because of the dipole forces) of the rate of fall of ε_∞ with increasing temperature.

We shall conclude by considering briefly the structure of the low-temperature phases of SnTe and GeTe which again have to be considered outside the harmonic approxi-
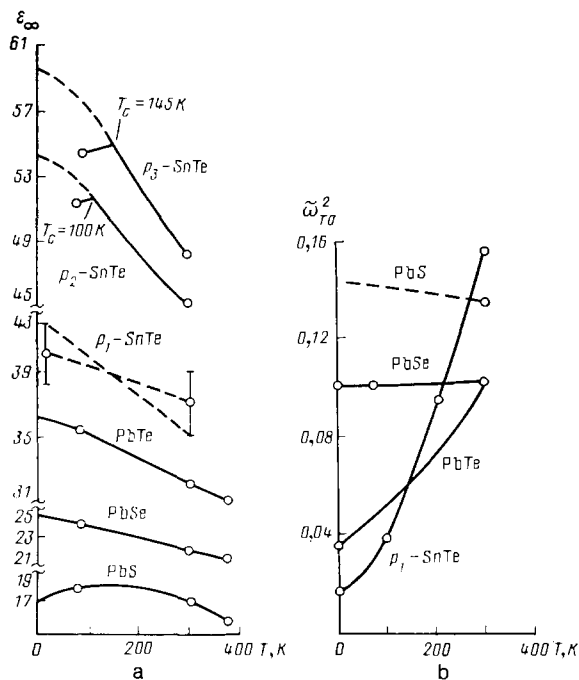
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FIG. 2. Temperature dependences of ε_∞ a) and $\tilde\omega_{TO}^2$ (b) obtained for lead chalcogenides (Ref. 129 and Table III) and SnTe (Refs. 110 and 130). In the case of SnTe the dependences ε_∞ (T) are shown for three compositions[110] with the following hole densities $p_1 = 8\times10^{20}$ cm^{-3}, $p_2 = 1.25\times10^{20}$, cm^{-3}, and $p_3 = 6\times10^{19}$ cm^{-3}, where $p_i = p_H^{(i)}$(77 K) (i = 1, 2, 3).

ture of which is close to that of a high-pressure phase observed for lead chalcogenides, for SnTe (Ref. 112), and also for GeTe itself,[131] but clearly distinct from the high-pressure phase.[17] The reason for the appearance of the γ phase in GeTe is not quite clear, because this is observed only in the case of a considerable deviation of the composition from stoichiometry and it is accompanied by the presence of high concentrations of lattice defects (vacancies in the germanium sublattice) and high densities of holes, and also by compression of the samples.[112] The latter may (like hydrostatic pressures) be responsible for the instability of TA phonons at the point X at the boundary of the Brillouin zone, which is favored by the low values of the TA(X) phonon frequencies in the cubic phases of IV–VI compounds,[132] and the observed difference between the structure of the γ phase of GeTe and its high-pressure phase is due to a strong inhomogeneity of the samples. It should be mentioned that hydrostatic compression of the lattice in crystals with a phonon instability at the boundary of the Brillouin zone increases T_c and in the case of crystals with a phonon instability at the center of the Brillouin zone, it reduces T_c (Ref. 133).

Clearly, we note that in our opinion the difference between the energies of possible low-temperature phases of IV–VI compounds is largely determined by the Coulomb electron-electron interaction and its inclusion is essential in a systematic calculation of the phase diagrams and it is essential also in accounting for the ferroelectric instability of the cubic phases of these compounds.

mation framework. A comparison of the energies of the ferroelectric phases of IV–VI compounds with various types of distortions (rhombohedral, triclinic, orthorhombic, and tetragonal) as a function of the degree of doping[12] or the hole density was made in Ref. 103 using the band approach. In fact, calculations were made of the difference between the band energies of the distorted structures and of the structure of a simple cube as a function of the hole density and this was done ignoring the ionicity, the electron-electron Coulomb interaction, the contribution of higher terms of the expansion of the electron-ion potential $\delta V_{ei}^{(m)}$ with $m > 1$, and the exchange-correlation contribution. In the absence of doping the rhombohedral phase observed experimentally for SnTe and GeTe is favored by the energy considerations. However, this solution (phase) becomes unstable as a result of doping (no matter how light) and changes to the triclinic, although the experimental results show that the rhombohedral phase is observed for SnTe right up to densities of the order of 4×10^{20} cm^{-3} (Ref. 114) and in GeTe right up to densities of the order of 7×10^{20} cm^{-3} (Ref. 112). The disagreement with the experimental results is explained in Ref. 103 by the characteristics of the model and of the electron spectra of the cubic phases of IV–VI compounds, mainly by the presence of pockets at the points L, which become filled with holes up to a certain density beginning from which the regions with a higher density of states are filled and this is understood to represent doping in the model proposed in Ref. 113. However, at hole densities higher than those given above it is found that SnTe becomes a virtual ferroelectric ($T_c < 0$ K) and in the case of GeTe slow cooling from temperatures above $T_c \sim 630$ K or prolonged annealing at temperatures below T_c produces a nonferroelectric (γ) phase[117] the struc-

5. CONCLUSIONS

We shall now summarize briefly this review. The existing microscopic theory of lattice dynamics allows us to understand qualitatively the nature of phonon instabilities in crystals and to obtain necessary quantitative estimates, including those based on calculations from first principles, i.e., without fitting parameters. The lattice stability is determined by adiabatic phonons, in contrast to the spectrum of corresponding resonance excitations for which the nonadiabaticity of the electron subsystem may be important. In calculations of the electron contribution to the matrix of the force constants this means that the lattice stability is governed by the static electron response to fields created as a result of displacement of nuclei from their equilibrium positions. A full allowance for the valence electrons to the matrix of the force constant must include lattice stabilizing and destabilizing terms. In discussing the influence of the valence electrons on the stability of some particular lattice vibration we must distinguish two situations, depending on whether this normal vibration is stable or unstable in a lattice of stripped ion cores. In the former case a strong destabilizing influence of electrons is responsible for the instability, whereas in the latter it is the weak stabilizing electron influence which has the same effect. In general, in the case of normal vibrations corresponding to "soft" modes of ferroelectrics and antiferroelectrics we can expect either situation. In the case of vibrations which are stable in a lattice of bare ion cores, for example, in the case of TO vibrations in diatomic cubic crystals, the conclusion about the dominant role of the electron contribution to the instability of these vibrations is trivial and it does not justify separation of any particular destabilizing electron contribution to account for

the lattice instability. An analysis made in the present review shows that separation of any particular electron contribution responsible for the lattice instability without specific estimates of the contribution of stripped ion cores can give incorrect results on the reasons for the lattice instability in ferroelectrics. An analysis of microscopic theories of the ferroelectric instability of IV–VI compounds demonstrates inconsistency of an analysis of the instability of TO(Γ) in the cubic phases of these compounds on the basis of the band energy approximation equivalent to the models utilizing the Fröhlich Hamiltonian with the interband electron-phonon interaction, and also obtained on the basis of an approximation utilizing the jellium model for calculation of the electron response. However, it should be pointed out that the search for the part of the total electron contribution responsible for the instability can be justified if the contribution of bare ion cores and the total electron contribution to the square of the frequency of TO vibrations is several times higher (and in the case of IV–VI compounds two orders of magnitude higher) than the observed values of this quantity and one can assume that this is due to the fact that some part of the electron contribution "destroys" almost completely the contribution of stripped ion cores, so that the remainder determines the observed frequency of TO vibrations. This does not mean that any separation of the total electron contribution into a sum of terms of different origin makes it possible to identify reliably the main contribution or that the physical nature of the main contribution will be the same for different divisions of the total effect. This ambiguity seems at first sight to hinder microscopic formulation of the criterion of the ferroelectric instability. In fact, discrimination between various representations of the electron contribution depends both on the investigation method (numerical calculations or a qualitative analysis) and on those characteristics of the electron structure and chemical binding or dielectric properties of the electron subsystem whose influence on the stability of TO vibrations is under discussion. For example, when we are dealing with the ferroelectric properties of IV–VI compounds it is useful to separate, using exact microscopic expressions, the contribution of the dipole forces to the frequency of TO vibrations. An analysis of the dipole mechanism of the ferroelectric instability of IV–VI compounds has made it possible to relate the ferroelectric properties of these compounds to the characteristics of dielectric properties of the electron subsystem, to the origin of the electron spectrum, and to special features of the chemical binding of the cubic phases of these compounds.

It should be pointed out that some topics in the microscopic theory of displacive ferroelectrics have been ignored in the present review or have not been dealt with sufficiently thoroughly. This applies particularly to the numerous shell models for the calculation of the phonon spectra, which have played an important role in the understanding of the microscopic theory of the ferroelectric instability,[16,17] and particularly it applies to the interesting model proposed by Bilz et al.[134,135] Moreover, we have ignored phase transitions in ternary compounds originating from IV–VI compounds, which exhibit a number of features that do not fit the concept of the purely phonon nature of the ferroelectric instability. In our opinion a more detailed analysis should be made of the microscopic theory of anharmonic effects in displacive ferroelectrics, but this would require a detailed account of

the relevant part of the microscopic theory of lattice dynamics in crystals, which is obviously outside the scope of the present review.

[1] The transition from normal (nonferroelectric) insulators, such as alkali halide crystals, to ferroelectric ones along the sequence normal insulator $\rightarrow$ virtual ferroelectric ($T_c < 0$ K) $\rightarrow$ ferroelectric ($T_c > 0$ K) not only results in softening of the frequency of critical TO vibrations at $T = 0$ K, but also in changes in the sign of the temperature coefficients of ω_{TO} and ε_0. This matched behavior of the frequencies obtained in the harmonic approximation and the temperature-dependent anharmonic correction to ω_{TO}^2 is clearly not accidental, but a theory based on a phenomenological lattice Hamiltonian cannot account for it.

[2] We shall consider only ferroelectrics which are cubic in the paraelectric phase, but this covers the majority of known displacive ferroelectrics.

[3] The long-wavelength limit $\mathbf{q} \rightarrow 0$ implies here and later the inequalities $q a_0 \ll 1$ and $qL \gg 1$, where L is the size of a crystal. In the case of crystals with the piezoelectric effect in the paraelectric phase the low-frequency range is assumed to be located above the range of piezoacoustic resonances: $\omega > v_{ac} q \gg v_{ac} L^{-1} \approx 10^4$–$10^5$ s^{-1} (Ref. 5).

[4] It can be shown[43,49,50] that the exact expression for the force matrix differs from that obtained above only in respect of the replacement of the static susceptibility $\tilde{\chi}(0)$ in the first term of Eq. (3.26), representing the contribution of $\delta V_{ne}^{(1)}$, with $\hat{\chi}(\omega)$ and in this case the second term in Eq. (3.26) representing the contribution of $\delta \hat{V}_{ne}^{(2)}$ is still expressed in terms of the static susceptibility $\hat{\chi}(0)$.

[5] The theory of Ref. 93 predicts that among IV–VI compounds the highest value of ε_∞ at $T = 0$ K in the cubic phase should be exhibited by GeTe, although ε_∞ for the low-temperature rhombohedral phase of GeTe (Ref. 109) with the composition characterized by $T_c \sim 700$ K is $\varepsilon_\infty(77 \text{ K}) = 34$ and $\varepsilon_\infty(295 \text{ K}) = 36$, i.e., it is less than for the cubic phase of SnTe (Ref. 110). It is shown in Refs. 93 and 111 that this can be explained by the different behavior of $\varepsilon_\infty(T)$ above and below T_c of IV–VI compounds.

[6] In the case of a strong deviation from stoichiometry in GeTe a γ phase is observed at temperatures $T < T_c = 630$ K (Refs. 117 and 118) and its structure is similar to that of the high-pressure phase observed in lead chalcogenides and in SnTe (Ref. 112).

[7] The ionicity is defined as the quantity representing the chemical inequivalence of atoms in two sublattices (for details see below). A rough measure of the ionicity is the difference between the ionization potentials of B and A atoms[105] (Table III).

[8] The purely ionic nature of E_{av} in compounds with the NaCl or CsCl structure is discussed by Harrison (see Chap. 18 in Ref. 92). In the case of IV–VI compounds this is a natural consequence of the origin of the electron spectrum and of the ionic-metallic nature of the chemical binding of the cubic phases of these compounds.

[9] It should be noted that we are speaking here not of the temperature dependences of the frequencies of the corresponding resonance excitations of the system, which can be strongly damped near T_c and are not known accurately, but of the temperature dependence of the elastic constant of the corresponding long-wavelength optical displacements [see Eq. (3.6) and the discussion that follows it].

[10] The pole structure of the expression for ε_∞ cannot by itself account for the observed sign of the temperature dependence $\partial \varepsilon_\infty / \partial T$. An analysis of the temperature dependence of ε_∞ of IV–VI compounds, needed to find the sign of $\partial \varepsilon_\infty / \partial T$, was made in Ref. 111. However, the existence of a pole structure has a considerable influence on the rate of change of ε_∞ with temperature, increasing this rate near a pole, i.e., it is important at sufficiently high values of ε_∞ ($T = 0$ K) (Ref. 121).

[11] The dependences $\varepsilon_\infty(T)$ shown in Fig. 2 for SnTe were taken from Ref. 110. As is now known, the values of $\varepsilon_\infty(77 \text{ K})$ for compositions with the Hall density of holes $p_H(77 \text{ K}) = 1.25 \times 10^{20}$ cm^{-3} and 6×10^{19} cm^{-3} correspond to the low-temperature phase of SnTe, since for these compositions the values of T_c are 100 K and 145 K (Refs. 114 and 115). At the transition point the permittivity ε_∞ has a kink with a maximum at $T = T_c$ (Ref. 93), which is allowed for in Fig. 2.

[12] More exactly, we are speaking here of self-doping, because the high densities of holes observed in SnTe and GeTe are due to the deviation of composition of these compounds in the homogeneity region in the direction of excess tellurium, i.e., these high densities are due to the presence of tin and germanium vacancies, respectively.[112]

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