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On nonadiabatic effects in phonon spectra of metals

E G Maksimov, A E Karakozov

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<u>Abstract.</u> Experimental and theoretical research on nonadiabatic effects in metals is briefly reviewed. It is shown that these effects are most manifest in optical phonon spectra at small wave vectors q satisfying the condition $qv_F < \omega_0(q)$, where v_F is the electron Fermi velocity, and $\omega_0(q)$ is the phonon frequency. Various theoretical approaches to calculating nonadiabatic effects are examined. Fröhlich's phenomenological fieldtheoretical model, the most widely used in such calculations, is discussed in detail, some aspects of its application are considered, and its efficiency as a tool for studying nonadiabatic effects is demonstrated.

1. Introduction

The concept of adiabatic separation of slow vibrational and fast electronic degrees of freedom was first introduced by Born and Oppenheimer [1]. The essence of the adiabatic approximation for calculating phonon spectra of crystals [2] is rather simple and can be formulated in the following way. To take into account the electron contribution to the phonon spectra, it suffices to calculate the electron response to the static ion density redistribution by considering the latter as an external field of a charge wave. Allowance made for the fact that ions actually vibrate at a finite velocity results, for most of the spectrum, in small corrections with respect to the parameter $\sqrt{m/M}$, where *m* and *M* are the electron and ion masses, respectively. The adiabatic approximation is ade-

E G Maksimov P N Lebedev Physical Institute, Russian Academy of Sciences, Leninskii prosp. 53, 119991 Moscow, Russian Federation Tel. (7-499) 135 75 11 Fax (7-499) 135 85 33 E-mail: maksimov@lpi.ru A E Karakozov L F Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Troitsk, Moscow region, Russian Federation Tel. (7-495) 334 05 82

Received 7 September 2007, revised 14 October 2007 Uspekhi Fizicheskikh Nauk **178** (6) 561–576 (2008) DOI: 10.3367/UFNr.0178.200806a.0561 Translated by N A Raspopov; edited by A Radzig quate in describing insulators and wide-gap semiconductors. The situation is much more complicated in metals [3]. Engelsberg and Schrieffer [4] were the first to notice that the magnitude of nonadiabatic effects may not be small for optical phonons with wave vectors satisfying the condition $\mathbf{q}\mathbf{v}_{\rm F} < \omega_0(\mathbf{q})$, where $\mathbf{v}_{\rm F}$ is the electron Fermi velocity, and $\omega_0(\mathbf{q})$ are bare frequencies for optical phonons. In this case, the nonadiabatic effects may result in appreciable (i.e., not proportional to $\sqrt{m/M}$ renormalization of phonon frequencies, strong dispersion of phonon frequencies at low q, and a finite linewidth of such phonons [5]. It should be mentioned, however, that the authors of paper [4] said nothing about the adiabaticity or nonadiabaticity of the corresponding phonons. A similar phenomenon has been observed in Raman scattering of light in some semiconductors and metals [5-8]. The adiabaticity problem was thoroughly considered in Ref. [9] for the normal state of metal. These effects may become even more important in the superconducting state at phonon frequencies $\omega_{\rm ph} \sim 2\Delta$, where \varDelta is the superconducting energy gap. Variation in the phonon frequencies and linewidths in a transition to the superconducting state was observed in the standard superconducting metal Nb [10]. The theory of nonadiabatic effects in superconductors was developed by Schuster [11] in the Bardeen-Cooper-Schrieffer (BCS) approximation, however, similarly to paper [4], without emphasizing the nonadiabaticity of the effects. In Ref. [4], a very interesting possibility for the phonon mode to split into two modes was predicted if the mode energy was close to the superconducting gap: $\omega_{\rm ph} \approx 2\Delta$. Later on, a similar effect was examined experimentally [12, 13].

Even earlier, in work by Migdal [14] the interrelation between electrons and phonons was studied in the framework of the Fröhlich field-theoretical model in more detail. In Ref. [14], the phonon frequencies were strongly renormalized due to electron – phonon interaction (EPI). In the work by Migdal, the renormalization actually arose in the framework of the adiabatic approach. This result and the very possibility of utilizing the Fröhlich model for describing the renormalization of phonon frequencies were repeatedly criticized [15– 17]. The existence of nonadiabatic effects in phonon spectra of metals was also criticized in Refs [18, 19], as well as in *Physics*–*Uspekhi* [20]. In this review, based on our work in this field [9, 21, 22] and on experimental and theoretical investigations of other authors, we will consider the nonadiabatic effects in phonon spectra of metals in more detail. Hereinafter, we use the system of atomic units ($e = m_e = \hbar = 1$).

2. Adiabatic approximation

Recall the principal items of the adiabatic approach [1, 2]. The criterion for system adiabaticity is the absence of excitations with energies on the order of ion vibration frequencies in its electronic spectrum. At first glance, this criterion is *a fortiori* broken in metals, because there are electron excitations with arbitrarily small energy near the Fermi surface. However, the number of such excitations in metals is rather small as compared to the total number of electrons, which makes it possible to employ the adiabatic approximation in determining the parameters that are integral over the electronic spectrum.

We can write down the total electron – ion Hamiltonian in the form

$$H = H_{\rm e}(\mathbf{r}) + H_{\rm i}(\mathbf{R}) + H_{\rm ei}(\mathbf{r}, \mathbf{R}). \qquad (2.1)$$

The adiabatic approach to the solution of the Schrödinger equation with Hamiltonian (2.1) implies that its eigenfunction $\Psi(\mathbf{r}, \mathbf{R})$ will be sought in the form of an expansion in the eigenfunctions $\psi(\mathbf{r}, \mathbf{R})$ of electron energy operator $H_{\rm e}(\mathbf{r}) + H_{\rm ei}(\mathbf{r}, \mathbf{R})$ for arbitrary ion configuration {**R**}:

$$\left[H_{\rm e}(\mathbf{r}) + H_{\rm ei}(\mathbf{r}, \mathbf{R})\right]\psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R})\psi_m(\mathbf{r}, \mathbf{R}), \qquad (2.2)$$

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_{m} \chi_m(\mathbf{R}) \psi_m(\mathbf{r},\mathbf{R}) \,. \tag{2.3}$$

Here, the functions $\chi_m(\mathbf{R})$ describing the properties of the ion subsystem can be found from the equations

$$[H_{i}(\mathbf{R}) + E_{m}(\mathbf{R})] \chi_{m}(\mathbf{R}) + \sum_{n} (A_{mn} + B_{mn}) \chi_{n}(\mathbf{R})$$
$$= E \chi_{m}(\mathbf{R}), \qquad (2.4)$$

where

$$A_{mn} = \frac{1}{M} \sum_{j} (\nabla_{\mathbf{R}_{j}})_{mn} \nabla_{\mathbf{R}_{j}}, \qquad B_{mn} = \frac{1}{M} \sum_{j} (\nabla_{\mathbf{R}_{j}}^{2})_{mn}, \quad (2.5)$$

 \mathbf{R}_j is the coordinate of the *j*th ion, and $(\nabla_{\mathbf{R}_j})_{mn}$ is a matrix element of gradient $\nabla_{\mathbf{R}_j}$ expanded in functions $\psi_m(\mathbf{r}, \mathbf{R})$. If the off-diagonal terms A_{mn} and B_{mn} in Eqn (2.4) are neglected, then we obtain two independent subsystems, namely, the electron subsystem described by Eqn (2.2), and the ion subsystem defined by Eqn (2.4). Equation (2.4) describing the vibrational spectrum of metal comprises the term $E_m(\mathbf{R})$ as a potential energy, which is the energy of electrons in a given static field of ions:

$$E_m(\mathbf{R}) = \left\langle H_e + \sum_n V_{ei}(\mathbf{r} - \mathbf{R}_n) \right\rangle.$$
(2.6)

Here, $V_{\rm ei}(\mathbf{r} - \mathbf{R}_n)$ is the electron-ion interaction potential. By expanding $H_{\rm i}(\mathbf{R})$ and $E_m(\mathbf{R})$ in an ordinary way near equilibrium positions of ions $\{\mathbf{R}_n^0\}$ in terms of the small deviations $\mathbf{u}_n = \mathbf{R}_n - \mathbf{R}_n^0$, one can obtain the expression for the force matrix $C_{nn'}^{\alpha\beta}$. In this case, the electron contribution to $C_{nn'}^{\alpha\beta}$ has the form

$$C_{nn'}^{\alpha\beta} = \frac{\partial^2 E_m}{\partial R_n^{\alpha} \partial R_{n'}^{\beta}} = \frac{\partial^2}{\partial R_n^{\alpha} \partial R_{n'}^{\beta}} \left\langle H_{\rm e} + \sum_m V_{\rm ei}(\mathbf{r} - \mathbf{R}_m) \right\rangle$$
$$= \frac{\partial}{\partial R_n^{\alpha}} \int \mathrm{d}^3 r \,\rho(\mathbf{r}) \,\frac{\partial}{\partial R_{n'}^{\beta}} \,V_{\rm ei}(\mathbf{r} - \mathbf{R}_{n'}) \,, \tag{2.7}$$

where $\rho(\mathbf{r})$ is the electron density. In writing out the last term in formula (2.7) we used the Hellmann–Feynman theorem. Finally, we can rewrite $C_{nn'}^{\alpha\beta}$ in the form

$$C_{nn'}^{\alpha\beta} = \int \mathrm{d}^3 r \, \frac{\partial}{\partial R_n^{\alpha}} \, \rho(\mathbf{r}) \, \frac{\partial}{\partial R_{n'}^{\beta}} \, V_{\mathrm{ci}}(\mathbf{r} - \mathbf{R}_{n'}) \\ + \, \delta_{nn'} \int \mathrm{d}^3 r \, \rho(\mathbf{r}) \, \frac{\partial^2}{\partial R_n^{\alpha} \, \partial R_n^{\beta}} \, V_{\mathrm{ci}}(\mathbf{r} - \mathbf{R}_n) \,.$$
(2.8)

One can see from expression (2.8) that the calculation of the electron contribution to the force matrix $C_{nn'}^{\alpha\beta}$ mainly reduces to the calculation of the derivative of electron density $\rho(\mathbf{r})$, because determination of the derivatives of electron–ion potential is not a particular problem. In the framework of the standard quantum perturbation theory, a derivative of $\rho(\mathbf{r})$ can be written out in the following form

$$\frac{\partial}{\partial \mathbf{R}_n} \rho(\mathbf{r}) = \int d^3 r' \, \chi(\mathbf{r}, \mathbf{r}', \omega = 0) \, \frac{\partial}{\partial \mathbf{R}_n} \, V_{\rm ei}(\mathbf{r} - \mathbf{R}_n) \,. \quad (2.9)$$

Here, $\chi(\mathbf{r}, \mathbf{r}', \omega = 0)$ is the static electron susceptibility in a crystal. The vibrational frequencies are determined in an ordinary way from the equation

$$\det \left| \overline{\Phi}^{\alpha\beta}(\mathbf{q}) - M\omega^2(\mathbf{q})\delta^{\alpha\beta} \right| = 0, \qquad (2.10)$$

where $\overline{\Phi}^{\alpha\beta}(\mathbf{q}) = \Phi^{\alpha\beta}(\mathbf{q}) - \Phi^{\alpha\beta}(0)$ is the dynamic vibrational matrix, which for a crystal with a single atom per unit cell is given by the following expression

$$\Phi^{\alpha\beta}(\mathbf{q}) = \frac{4\pi e^2 Z^2}{\Omega_0} \sum_{\mathbf{G}} \frac{(\mathbf{q} + \mathbf{G})^{\alpha} (\mathbf{q} + \mathbf{G})^{\beta}}{(\mathbf{q} + \mathbf{G})^2} + \frac{1}{\Omega_0} \sum_{\mathbf{GG}'} (\mathbf{q} + \mathbf{G})^{\alpha} (\mathbf{q} + \mathbf{G}')^{\beta} V_{\text{ei}}(\mathbf{q} + \mathbf{G}) \times \chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega = 0) V_{\text{ei}}(\mathbf{q} + \mathbf{G}'). \quad (2.11)$$

The first summand in expression (2.11) is a contribution of lattice ions to the dynamic vibrational matrix, and the second summand is determined by the electron system in a periodical lattice field. Here, Z is the ion charge, G, G' are the vectors of reciprocal lattice, $V_{ei}(\mathbf{q} + \mathbf{G})$ is the matrix element for electron-ion interaction, $\chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega = 0)$ is the Fourier component of static electron susceptibility, which is an infinite-dimensional matrix in the space of reciprocal lattice vectors **G**, **G**', and, finally, Ω_0 is the unit cell volume. The consistent multiparticle theory of lattice dynamics resulting in formulas (2.9)-(2.11) was developed in 1960s-1970s (see, e.g., reviews [23, 24]), however, no consistent microscopic calculations of crystal phonon spectra were made in the framework of this approach. We may only mention the calculations of lattice dynamics for simple metals in the framework of the perturbation theory for the small electronic – ionic pseudopotential (see review [16]). The difficulties in the phonon calculations by formulas (2.9)-(2.11) are mainly related to the calculation of the electron

susceptibility matrix. However, it should be noted that expression (2.11) for the electron contribution to the dynamic vibrational matrix is general and absolutely rigorous in the adiabatic and harmonic approximations, which has proved to be rather useful in solid-state theory. Many rigorous and exact relationships in lattice dynamics were established by using this expression and numerous approximate and semiphenomenological approaches to the calculation of phonon spectra in crystals [16, 23, 24] were developed. In particular, certain problems were solved concerning the instability of phonon excitations due to anomalies in the electronic spectra, namely, so-called nesting [21]. We will revert to the calculation problem for electron susceptibility matrix in Section 4, which is devoted to the microscopic theory of lattice dynamics. We would like to emphasize here the fact that the success of the linear response theory in the method of the density functional allowed escaping the computation of the electron susceptibility matrix at all, while finding the phonon spectra in the adiabatic approximation. In the framework of this approach, one can directly calculate the derivative of electron density distribution $\rho(\mathbf{r})$, which, in accordance with formula (2.8), determines the electron contribution to a force matrix of a crystal (see reviews [25, 26]).

In the framework of the adiabatic approximation, the electron – phonon interaction is included in the off-diagonal summands A_{mn} and B_{mn} of Eqn (2.4). According to Browman and Kagan [15, 16], this interaction can be taken into account in the following way. With the perturbation theory we can calculate nonadiabatic correction ΔE to the total energy of the system. Then, by varying energy over the corresponding occupation numbers we obtain the corrections to the phonon $(\omega_{q\lambda})$ and electron (ε_k) energies:

$$\delta\omega_{\mathbf{q}\lambda} = \frac{\delta(\Delta E)}{\delta N_{\mathbf{q}\lambda}}, \quad \delta\varepsilon_{\mathbf{k}} = \frac{\delta(\Delta E)}{\delta n_{\mathbf{k}}}.$$
 (2.12)

Taking into account the fact that

$$(\nabla_{\mathbf{R}_{i}})_{mn} = -\frac{\left[\nabla_{\mathbf{R}_{i}}H_{\mathrm{ei}}(\mathbf{r},\mathbf{R})\right]_{mn}}{E_{m}-E_{n}},$$

and passing to the momentum representation for electrons and phonons, one can show [15, 16] that

$$\delta\omega_{\mathbf{q}\lambda} = \sum_{\mathbf{k}} |M_{\mathbf{k}\mathbf{q}\lambda}|^2 \frac{n_{\mathbf{k}} - n_{\mathbf{k}+\mathbf{q}}}{E_{\mathbf{k}} - E_{\mathbf{k}+\mathbf{q}} - \omega_{\mathbf{q}\lambda} + \mathrm{i}\delta} - \sum_{\mathbf{k}} |M_{\mathbf{k}\mathbf{q}\lambda}|^2 \frac{n_{\mathbf{k}} - n_{\mathbf{k}+\mathbf{q}}}{E_{\mathbf{k}} - E_{\mathbf{k}+\mathbf{q}}}, \qquad (2.13)$$

where $M_{kq\lambda}$ is the matrix element for the operator

$$\sum_{j} \left[\nabla_{\mathbf{R}_{j}} H_{\mathrm{ei}}(\mathbf{r}, \mathbf{R}) \right]_{mn}.$$

It is easy to verify from (2.13) that for the greater part of the phonon spectrum satisfying condition $\mathbf{qv}_{\mathrm{F}} > \omega_{\mathbf{q}\lambda}$ the corrections caused by nonadiabatic effects are as small as

$$\Delta \omega_{\mathbf{q}\lambda} = \operatorname{Re} \delta \omega_{\mathbf{q}\lambda} \approx \omega_{\mathbf{q}\lambda} \left(\frac{\overline{\omega}}{\varepsilon_{\mathrm{F}}}\right)^{2}, \qquad \Gamma_{\mathbf{q}\lambda} = \operatorname{Im} \delta \omega_{\mathbf{q}\lambda} \approx \omega_{\mathbf{q}\lambda} \frac{\overline{\omega}}{\varepsilon_{\mathrm{F}}}.$$
(2.14)

Here, $\overline{\omega}$ is the quantity on the order of the mean phonon frequency. It was stressed by Brovman and Kagan [15, 16] that the smallness of nonadiabatic renormalization of

phonon frequencies for $\mathbf{qv}_{\mathrm{F}} > \omega_{\mathbf{q}\lambda}$ arises due to a mutual compensation of two summands in formula (2.13), though the summands themselves are not small in $\sqrt{m/M}$. For the acoustic spectrum, the condition $\mathbf{qv}_{\mathrm{F}} > \omega_{\mathbf{q}\lambda}$ holds over the whole Brillouin zone. However, the first summand in formula (2.13) vanishes for optical phonons at small wave vectors \mathbf{q} . In the range of the wave vectors meeting the condition $\mathbf{qv}_{\mathrm{F}} < \omega_{\mathbf{q}\lambda}$, the second summand results in the strong renormalization of adiabatic phonon frequencies:

$$\delta\omega(\mathbf{q}=0) = \int \frac{d^3k}{(2\pi)^3} M^2(\mathbf{k}, \mathbf{q}=0) \,.$$
 (2.15)

Unfortunately, it is difficult to obtain an exact expression for the matrix element $M(\mathbf{k}, \mathbf{q})$ in the frameworks of the adiabatic approach. Simple model estimations of expression (2.15) show that $\delta \omega \approx \lambda \langle \omega_{ad} \rangle$ [17], where λ is the constant of electron-phonon interaction, and $\langle \omega_{ad} \rangle$ is the mean adiabatic frequency of optical phonons.

We obtain the following expression for renormalization of the electronic spectrum:

$$\Delta E_{\mathbf{k}} = \sum_{\mathbf{q}\lambda} |M_{\mathbf{k}\mathbf{q}\lambda}|^2 \frac{\omega_{\mathbf{q}\lambda}(1-2n_{\mathbf{k}+\mathbf{q}})}{(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})^2 - \omega_{\mathbf{q}\lambda}^2} \,. \tag{2.16}$$

One can readily see that expression (2.16) is not small for electrons near the Fermi surface, and falls as they move away from it. In particular, the nonadiabatic interaction determines the energy relaxation in metals and their superconducting properties. Based on the formulas for the adiabatic approximation given above, one can make the following conclusions concerning the role of electron-phonon interaction in metals.

(1) If inequality $\mathbf{qv}_F > \omega_{\mathbf{q}\lambda}$ is met, then the dynamic interaction between electrons and phonons, arising due to the nonadiabatic corrections A_{mn} and B_{mn} , weakly renormalizes the phonon spectrum. Hence, phonon frequencies in metals can be calculated in the framework of the adiabatic approximation with an accuracy on the order of $\sqrt{m/M}$ for the greater part of the Brillouin zone.

(2) Subject to the following inequality $\mathbf{q}\mathbf{v}_{\mathrm{F}} < \omega_{\mathbf{q}\lambda}$, the frequencies of optical phonons are strongly renormalized due to nonadiabatic corrections which should be taken into account in all calculations involving such phonons.

(3) Renormalization of electrons near the Fermi surface, caused by nonadiabatic electron-phonon interaction, is strong and substantial in describing many physical phenomena occurring in an electron system.

(4) Instability of the system in the framework of the adiabatic approximation shows its worth in the appearance of negative values of $\omega_{q\lambda}^2$ in adiabatic equation (2.10).

A particular discussion concerning the reasons for these instabilities and their possible connection with electron– phonon interaction will be postponed until the next section. It is worth noting here that due to the non-Hamiltonian character and lack of convenient diagram techniques for calculating the corresponding corrections, the adiabatic approximation can hardly be used for self-consistent computations of electron and phonon systems.

3. Nonadiabatic effects in the Fröhlich model

Most works investigating nonadiabatic effects in both normal and superconducting states of metal have been carried out in the framework of the Fröhlich model. The Hamiltonian of this model can be written out in the form [27]

$$H = \sum_{\mathbf{p},\sigma} \xi_{\mathbf{p}} c_{\mathbf{p}\sigma}^{+} c_{\mathbf{p}\sigma} + \sum_{\mathbf{p},\mathbf{q},\sigma,s} g_{s}(\mathbf{p},\mathbf{q}) c_{\mathbf{p}+\mathbf{q},\sigma}^{+} c_{\mathbf{p}\sigma}(b_{\mathbf{q}s} + b_{-\mathbf{q}s}^{+})$$

+
$$\sum_{\mathbf{q}s} \omega_{0}(\mathbf{q},s) \left(b_{\mathbf{q}s}^{+} b_{\mathbf{q}s} + \frac{1}{2} \right), \qquad (3.1)$$

where $c_{\mathbf{p}\sigma}^+$ and $c_{\mathbf{p}\sigma}$ are the electron creation and annihilation operators, $\xi_{\mathbf{p}}$ is the electron spectrum counted off from the chemical potential, $g_s(\mathbf{p}, \mathbf{q})$ is the matrix element for EPI, and $b_{\mathbf{q}s}^+$ and $b_{\mathbf{q}s}$ are the creation and annihilation operators for the phonon mode *s* with the momentum **q** and energy $\omega_0(\mathbf{q}, s)$.

The expression for the phonon Green function $D_s(\mathbf{q}, \omega)$ can be written in the form

$$D_s^{-1}(\mathbf{q},\omega) = \omega_0^{-2}(\mathbf{q},s) \left[\omega^2 - \omega_0^2(\mathbf{q},s) \right] - \Pi_s(\mathbf{q},\omega) , \quad (3.2)$$

where $\Pi_s(\mathbf{q}, \omega)$ is the polarization operator. The phonon frequency $\omega(\mathbf{q}, s)$ renormalized due to EPI is derived according to expression (3.2) from the equation

$$\omega^{2}(\mathbf{q},s) = \omega_{0}^{2}(\mathbf{q},s) \left\{ 1 + \operatorname{Re} \Pi_{s} \left[\mathbf{q}, \omega(\mathbf{q},s) \right] \right\}.$$
(3.3)

In the simplest single-loop approximation, by using the electron Green functions for free particles and assuming $g_s(\mathbf{p}, \mathbf{q}) \approx g$, we obtain the following expression for the polarization operator

$$\Pi(\mathbf{q},\omega) = 2g^2 \sum_{\mathbf{p}} \frac{n_{\mathbf{p}} - n_{\mathbf{p}+\mathbf{q}}}{\omega - \xi_{\mathbf{p}+\mathbf{q}} + \xi_{\mathbf{p}} + \mathrm{i}\delta} \,. \tag{3.4}$$

Consider now the behavior of phonon modes $\omega(\mathbf{q}, s)$ in the two limiting cases: $\mathbf{q}\mathbf{v}_{\mathrm{F}} \ge \omega_0(\mathbf{q}, s)$, and $\mathbf{q}\mathbf{v}_{\mathrm{F}} \ll \omega_0(\mathbf{q}, s)$. In the first case, we obtain the well-known expression that coincides with the formula prepared by Migdal [14]:

$$\omega^{2}(\mathbf{q}) = \omega_{0}^{2}(\mathbf{q}, s) \left[1 - 2g^{2}N(0) \right].$$
(3.5)

The quantity $g^2 N(0)$ represents the dimensionless EPI constant

$$\lambda = g^2 N(0) \,. \tag{3.6}$$

In metals, coupling constant (3.6) is not usually small and can be on the order of unity. Hence, it follows from relationships (3.5), (3.6) that EPI strongly renormalizes phonon frequencies. Migdal thoroughly considered the case of acoustic phonons, for which the condition $\mathbf{q}\mathbf{v}_{\mathrm{F}} \gg \omega_0(\mathbf{q}, s)$ always holds, and obtained just the same result. We have already mentioned that this result obtained by Migdal was instantaneously criticized on the grounds that it contradicts the adiabatic approximation in which, as we have just shown, nonadiabatic EPI does not renormalize acoustic phonons. This criticism might be correct if anyone could show that the frequency $\omega_0(\mathbf{q}, s)$ in the Fröhlich Hamiltonian is just the adiabatic phonon frequency. The fact is that the Fröhlich Hamiltonian, similarly to any model system, implies, in contrast to an exact Hamiltonian, an optimal (based on intuition or experiment) choice of bare quasiparticles and interaction constants, at which such a simplified model has physical meaning. Later on, we will revert to a discussion on the possible physical meaning of the Fröhlich model and the parameters involved. For the reasons given below, we now make the convention that the quantity $\omega^2(\mathbf{q}) = \omega_0^2(\mathbf{q}, s)(1-2\lambda)$ may be considered the adiabatic phonon frequency, and systems with $\lambda < 1/2$ will be concerned.

Let us consider here the renormalization of optical phonons in the Fröhlich model confining ourselves, for simplicity, to zero-dispersion bare phonons with the frequency $\omega_0^2(\mathbf{q}, s) = \omega_0^2$, similarly to paper [4]. At large wave vectors \mathbf{q} meeting the conditions $\mathbf{qv}_F \ge \omega_0$ and $q \le k_F$, the phonon frequency is renormalized according to expression (3.5) in the following way:

$$\omega^2(\mathbf{q}) = \omega_0^2 \left[1 - 2g^2 N(0) \right]. \tag{3.7}$$

For small wave vectors $q \rightarrow 0$, from formulas (3.3) and (3.4) it follows that $\Pi_s(\mathbf{q} = 0, \omega) = 0$ — that is, the phonon frequency is not renormalized in this case:

$$\omega^2(q \to 0) = \omega_0^2 \,. \tag{3.8}$$

One can see from (3.7) and (3.8) that the frequency of optical phonons with $q \rightarrow 0$ may be noticeably higher than the frequencies of phonons with large wave vectors $q > \omega_0/v_{\rm F}$. The difference $\Delta\omega^2 = \omega^2(\mathbf{q} = 0) - \omega^2(q > \omega_0/v_{\rm F})$ in these frequencies is not small in the nonadiabatic parameter $\sqrt{m/M}$:

$$\Delta \omega^2 = 2\lambda \omega_0^2 \,. \tag{3.9}$$

As we have already agreed earlier, we will consider the frequency in formula (3.7) for $\mathbf{qv}_{\mathrm{F}} \ge \omega_0$ as adiabatic, whereas at q = 0 we assume it renormalized by a nonadiabatic interaction. Thus, for the weak coupling we obtain the expression $\omega_{\mathrm{nonad}}^2 \approx \omega_{\mathrm{ad}}^2 + 2\lambda\omega_{\mathrm{ad}}^2$, which is absolutely the same as in the case of the adiabatic approach [see formulas (2.13), (2.15)]. The only difference resides in the redesignation of the adiabatic frequency, in which allowance was made for the coupling between the bare spectrum of the Fröhlich Hamiltonian and the adiabatic spectrum of the $\omega_{\mathrm{ad}}^2(\mathbf{q},s) = \omega_0^2(\mathbf{q},s)(1-2\lambda)$ type. The coupling constant λ will be estimated later in Section 4.

We can also evaluate the dispersion of the optical phonon for $\mathbf{q}\mathbf{v} \leq \omega_0$ by writing the expression for $\Pi(\mathbf{q}, \omega)$ in the form [9]

$$\Pi(\mathbf{q},\omega) = 2g^2 \int \frac{\mathrm{d}S_{\mathrm{F}}}{v_{\mathrm{F}}} \frac{\mathbf{q}\mathbf{v}_{\mathrm{F}}}{\omega - \mathbf{q}\mathbf{v}_{\mathrm{F}} + \mathrm{i}\delta} \,. \tag{3.10}$$

Here, the integral is taken over the Fermi surface. For the quantity $\omega^2(\mathbf{q})$ we have

$$\omega^2(\mathbf{q}) = \omega_0^2 + a\lambda (\mathbf{q}\bar{\mathbf{v}}_{\mathrm{F}})^2 \,. \tag{3.11}$$

Here, *a* is a constant on the order of unity, and \bar{v}_F is the mean Fermi velocity. Hence, one can see that at small wave vectors the dispersion of optical phonons may considerably exceed the ordinary speed of sound in metals and may be comparable with the Fermi velocity. One can also calculate the phonon linewidth:

$$\gamma(\mathbf{q},\omega) = 2g^2 \int \frac{\mathrm{d}S_{\mathrm{F}}}{v_{\mathrm{F}}} \,\delta(\omega - qv_{\mathrm{F}})\,. \tag{3.12}$$

From this formula it follows that at T = 0 the linewidth of optical phonons vanishes at q = 0. There is a threshold at $\omega \approx (\mathbf{qv}_{\mathrm{F}})_{\min}$ and a maximum at $\omega \approx \mathbf{q}\bar{\mathbf{v}}_{\mathrm{F}}$.

As a matter of fact, just these effects, namely, the large difference between optical phonon frequencies at $\mathbf{q} = 0$ and for $q > \omega_0/v_{\rm F}$, which is independent of the nonadiabatic parameter $\sqrt{m/M}$, and the presence of strong dispersion for the phonon mode at $\mathbf{qv}_{\rm F} \cong \omega_0$, have been subsequently termed the nonadiabatic effects. Similar effects were studied theoretically in Refs [4, 9, 28–30] (see also review [5]). In addition to the nonadiabatic renormalization of the optical phonon frequency at $\mathbf{q} = 0$ and the change in the dispersion of these phonons at small \mathbf{q} , one can also evaluate the temperature variations for the nonadiabatic effects. To this end, one should take into account the variation in the electron Green function due to EPI in calculating the polarization operator [9].

The influence of conduction electrons on longitudinal optical modes in semiconductors and ordinary metals has been examined experimentally [5]. In most experimental works on doped semiconductors [5], a sufficiently trivial phenomenon was mainly observed, which was mentioned in an early work [28]. It was the vanishing of the frequency splitting for longitudinal and transverse optical modes at $\mathbf{q} = 0$, when free charge carriers were injected into an ionic crystal. In doped semiconductors and metals, variations in phonon frequencies and linewidths were also observed [5, 10, 31].

The most impressive experimental results on nonadiabatic effects in phonon spectra of metals were obtained by Ponosov and co-authors [6-8]. It is usually believed that Raman scattering is used to measure the frequencies of optical phonons at the wave vectors q = 0. Actually, in measuring Raman scattering by laser radiation with different energies, the phonons are excited with different, even if small, finite vectors **q**. Ponosov and co-authors [6-8] suggested a method capable of measuring the phonon frequencies and dispersion at the wave vectors $q\cong\omega_{
m ph}/v_{
m F},$ as well as the phonon linewidth. In addition, the dependence of these quantities on temperature was also studied. In Fig. 1, the measured dispersion of optical phonons and their linewidths in metal osmium are shown. The results obtained agree well qualitatively with the theoretical predictions made in Ref. [9]. A possible quantitative description of these experiments will be discussed in Section 4.

In the above-given consideration of the nonadiabatic effects in the Fröhlich model, the simplest single-loop approximation was used for the polarization operator. As early as in work by Migdal [14] it was stressed that in calculating the polarization operator at small wave vectors **q** one should take into account vertex corrections. Similar results have been obtained by other authors [4, 9, 29, 30]. It was mentioned that these corrections to the polarization operator for $qv \leq \omega_{ph}$ are not small with respect to the parameter $\sqrt{m/M}$. Such corrections result, first, in a trivial quantitative change in certain results discussed above, in particular, for the parameter a in the phonon dispersion (3.11). We use the term 'trivial' because even without taking into account the vertex corrections we do not know the exact values of all the parameters in the Fröhlich model. Hence, there are no reasons to calculate an additional renormalization for them. However, more significant effects may arise due to the vertex corrections. One of them was predicted even by Engelsberg and Schrieffer [4].



Figure 1. The experimental linewidth (a) and frequency (b) of the phonon E_{2g} along the symmetric directions of the Brillouin zone (taken from Ref. [8]).

Having calculated the second-order vertex function with respect to small momenta **q**, they showed that the zerodispersion optical phonon mode may split into two modes $\omega^2(\mathbf{q}) = \omega_0^2 \pm c(\mathbf{q}\mathbf{v}_F)^2$, where c is a parameter expressed via the electron – phonon coupling constant. No such phenomenon has been discovered experimentally. Moreover, after issuing paper [4] this question was only briefly discussed in work [30] and it is still not clear whether the splitting of the optical mode is a consequence of the approximations made in paper [4] or will take place in more exact calculations. It is worth noting that similar splitting of phonon modes is truly observed in superconductors. The vertex corrections also result in one more nontrivial consequence which we prefer to discuss in the following by the example of nonadiabatic effects in the superconducting state.

Phonon frequencies in the superconducting state are still determined by expression (3.2). The polarization operator in the superconducting state [32] is an analytic continuation of the expression

$$\hat{H}_{s}(\mathbf{q}, \mathrm{i}\omega_{n}) = T \sum_{m, \mathbf{p}} g_{s}(\mathbf{p}, \mathbf{q}) \operatorname{Tr} \left[\hat{\tau}_{3} \hat{G}(\mathbf{p} + \mathbf{q}, \mathrm{i}\omega_{m} + \mathrm{i}\omega_{n}) \right.$$
$$\times \hat{\Gamma}_{s}(\mathbf{p} + \mathbf{q}, \mathrm{i}\omega_{m} + \mathrm{i}\omega_{n}, \mathbf{p}, \mathrm{i}\omega_{m}) \hat{G}(\mathbf{p}, \mathrm{i}\omega_{m}) \right], \qquad (3.13)$$

where $\omega_m = \pi T(2m + 1)$, $\hat{G}(\mathbf{p}, i\omega_n)$ is the Green function for electrons in Nambu representation, and $\hat{\Gamma}_s$ is the matrix vertex part satisfying the equation of the Bethe–Salpeter type. In the Fröhlich model, the electron–electron interaction giving rise to superconductivity is EPI, which is expressed via the Green function for phonons and depends on momenta and energy. It is will known that in the case of weak coupling the Eliashberg theory [33] for superconductors with EPI reduces to the BCS model. We will restrict ourselves just to this approximation. The effects of strong electron–phonon coupling will be considered in this section below. In the framework of the BCS model, the vertex part $\hat{\Gamma}_s$ satisfies the equation of the type

$$\Gamma_{s}(\mathbf{p}+\mathbf{q},i\omega_{m}+i\omega_{n},\mathbf{p},i\omega_{m}) = g_{s}(\mathbf{p}+\mathbf{q},\mathbf{p})\hat{\tau}_{3}$$
$$-T\sum_{m',\mathbf{p}'}\hat{\tau}_{3}\hat{G}(\mathbf{p}',i\omega_{m'})\hat{\Gamma}_{s}(\mathbf{p}'+\mathbf{q},i\omega_{m'}+i\omega_{n},\mathbf{p}',i\omega_{m'})$$
$$\times\hat{G}(\mathbf{p}'+\mathbf{q},i\omega_{m'}+i\omega_{n})\hat{\tau}_{3}V(\mathbf{p}',\mathbf{p}), \qquad (3.14)$$

where the electron–electron interaction potential $V(\mathbf{p}', \mathbf{p})$ simulates the behavior of combined electron–phonon and Coulomb interactions in the range of energies $\omega \leq \omega_c$:

$$V(\mathbf{p}', \mathbf{p}) \approx -\sum_{sL} g_{sL}^2 \Psi_L^*(\mathbf{p}') \Psi_L(\mathbf{p}) \Theta\left(\omega_{\rm c} - |\xi_{\mathbf{p}}|\right) \Theta\left(\omega_{\rm c} - |\xi_{\mathbf{p}'}|\right).$$
(3.15)

Here, ω_c is the cut-off energy equal by order of magnitude to the characteristic phonon energy $\langle \Omega_{ph} \rangle$, and Ψ_L is a complete set of orthogonal functions. The latter can be chosen, for example, as Fermi-surface Allen harmonics [34]. Their particular form is not important for our purposes. The Green function for electrons in the BCS model is given by

$$\hat{G}(\mathbf{p}, \mathrm{i}\omega_n) = -\frac{\mathrm{i}\omega_n \hat{\tau}_0 + \mathcal{A}_{\mathbf{p}} \hat{\tau}_1 + \xi_{\mathbf{p}} \hat{\tau}_3}{\omega_n^2 + \mathcal{A}_{\mathbf{p}}^2 + \xi_{\mathbf{p}}^2}, \qquad (3.16)$$

where $\xi_{\mathbf{p}}$ is the spectrum of single-electron excitations, and $\Delta_{\mathbf{p}}$ is the superconducting gap that satisfies the principal BCS equation

$$\hat{\tau}_3 \Delta_{\mathbf{p}} = -T \sum_{n\mathbf{p}'} \hat{\tau}_3 \hat{G}(\mathbf{p}', \mathbf{i}\omega_n) \hat{\tau}_2 \Delta_{\mathbf{p}'} \hat{\tau}_3 V(\mathbf{p}', \mathbf{p}) \,. \tag{3.17}$$

The matrix vertex part $\hat{\Gamma}_s$ in equation (3.14) may be written out in the form

$$\hat{\Gamma}_s = \Gamma_s^{(2)} \hat{\tau}_2 + \Gamma_s^{(3)} \hat{\tau}_3 \,, \tag{3.18}$$

where

-(3)

$$\Gamma_s^{(2,3)}(\mathbf{p}',\mathbf{p}) = \sum_L \Gamma_{sL}^{(2,3)} \Psi_L^*(\mathbf{p}') \Psi_L(\mathbf{p}) \,.$$

In the simplest case of isotropic s-pairing, the energy gap $\Delta_{\mathbf{p}}$ will have only one harmonic with L = 0:

$$\Delta_{\mathbf{p}} = \Psi_{L=0}(\mathbf{p})\Delta_{L=0} \,. \tag{3.19}$$

In the framework of the standard approximations for the BCS model given above, the vertex function only depends on the transferred momentum and energy; thus, Eqn (3.14) can be solved exactly. The analytic continuation for the solution (3.14) has a simple, though lengthy, form. The result is as follows:

$$\Gamma_{sL}^{(2)}(\mathbf{q},\omega) = g_{sL}(\mathbf{q}) \frac{\mathrm{i}g_L^2 I_2^L(\mathbf{q},\omega)}{\left[1 + g_L^2 I_3^L(\mathbf{q},\omega)\right] \left[1 - g_L^2 I_1^L(\mathbf{q},\omega)\right] + \left[g_L^2 I_2^L(\mathbf{q},\omega)\right]^2},$$
(3.20)

$$\Gamma_{sL}^{(c)}(\mathbf{q},\omega) = g_{sL}(\mathbf{q}) \\
\times \left(1 - \frac{g_L^2 I_3^L(\mathbf{q},\omega) - g_L^4 \{I_1^L(\mathbf{q},\omega) I_3^L(\mathbf{q},\omega) - [I_2^L(\mathbf{q},\omega)]^2\}}{[1 + g_L^2 I_3^L(\mathbf{q},\omega)] [1 - g_L^2 I_1^L(\mathbf{q},\omega)] + [g_L^2 I_2^L(\mathbf{q},\omega)]^2}\right),$$
(3.21)

where the notations $g_{sL}(\mathbf{q}) = g_{sL}\Psi_L(\mathbf{q})$, $\Gamma_{sL}^{(2,3)}(\mathbf{q},\omega) = \Gamma_{sL}^{(2,3)}(\omega)\Psi_L(\mathbf{q})$, and $g_L^2 = \sum_s g_{sL}^2$ were introduced. The explicit form of functions $I_j^L(\mathbf{q},\omega)$ for each value of j = 1, 2, 3 is determined by a combination of indices α , β , γ in the integral

$$I_{\alpha\beta\gamma}^{L}(\mathbf{q},\omega) = \frac{1}{4} \sum_{\mathbf{p}} |\Psi_{L}(\mathbf{p})|^{2} \tanh\left(\frac{E_{\mathbf{p}}}{2T}\right) \\ \times \left[M_{\alpha\beta\gamma}^{+}K^{-}(\mathbf{p}+\mathbf{q},\mathbf{p},\omega) + M_{\alpha\beta\gamma}^{-}K^{+}(\mathbf{p}+\mathbf{q},\mathbf{p},\omega)\right] \mathcal{O}(\omega_{c} - |\xi_{\mathbf{p}}|),$$
(3.22)

which comprises the coherence factors

$$M_{\alpha\beta\gamma}^{\pm} = \alpha \pm \frac{\beta \Delta^2 + \gamma \xi_{\mathbf{p}+\mathbf{q}} \xi_{\mathbf{p}}}{E_{\mathbf{p}+\mathbf{q}} E_{\mathbf{p}}}$$
(3.23)

and functions

$$K^{\pm}(\mathbf{p}+\mathbf{q},\mathbf{p},\omega) = \frac{1}{E_{\mathbf{p}+\mathbf{q}} \pm E_{\mathbf{p}} + \omega + \mathrm{i}\delta} + \frac{1}{E_{\mathbf{p}+\mathbf{q}} \pm E_{\mathbf{p}} - \omega - \mathrm{i}\delta}$$

Here, $E_{\mathbf{p}} = (\xi_{\mathbf{p}}^2 + \Delta^2)^{1/2}$ is the spectrum of quasiparticles in a superconductor. Indices *j* in functions $I_j^L(\mathbf{q}, \omega)$ correspond to the following combinations of α , β , γ in formulas (3.22) and (3.23):

$$j = 1 \quad \alpha = 1, \quad \beta = -1, \quad \gamma = -1,$$

$$j = 2 \quad \alpha = 0, \quad \beta = \frac{\omega}{\Delta}, \quad \gamma = 0,$$

$$j = 3 \quad \alpha = 1, \quad \beta = -1, \quad \gamma = 1.$$
(3.24)

The expressions obtained for the vertex functions are similar in form to those obtained in works [35-37] in the calculations of dielectric response in a superconductor. Having used the results of these works, one can show that in the framework of the adiabatic approximation — that is, at $\omega = 0$ — superconductivity has a negligible effect, whose magnitude is of order $(\Delta/\epsilon_F)^2$, on phonon frequencies. In our consideration, however, we make no allowance for long-range Coulomb interaction which, as we will ascertain, has no direct influence on the nonadiabatic phenomena under study.

The expression for the *L*th harmonics of the phonon selfenergy is given by

$$\Pi_{sL}(\mathbf{q},\omega) = -2g_L^2 \tilde{I}_3^L(\mathbf{q},\omega) - 2g_L^2 \frac{I_3^L(\mathbf{q},\omega) [1 - g_L^2 I_1^L(\mathbf{q},\omega)] + g_L^2 [I_2^L(\mathbf{q},\omega)]^2}{[1 + g_L^2 I_3^L(\mathbf{q},\omega)] [1 - g_L^2 I_1^L(\mathbf{q},\omega)] + [g_L^2 I_2^L(\mathbf{q},\omega)]^2}.$$
(3.25)

Here, function $\overline{I}_{3}^{L}(\mathbf{q},\omega)$ is also determined by an integral of the (3.13) type but with $\Theta(\omega_{c} - |\xi_{p}|)$ replaced by $\Theta(|\xi_{p}| - \omega_{c})$. This function describes the contribution of EPI to the self-energy of phonons from the domains distant from the Fermi surface. Hence, the expression for $\widetilde{I}_{3}^{L}(\mathbf{q},\omega)$ is completely independent of the superconductivity parameters, and we may put the superconducting gap Δ to zero in the related calculations. The formulas obtained above completely describe systems with s-pairing for all values of wave vectors \mathbf{q} and frequencies ω . They may be utilized in studying nonadiabatic effects in quasiisotropic systems and investigating phonon modes near Kohn anomalies, in particular, in systems with nesting. Let us consider the limiting case of $\mathbf{q} = 0$ and T = 0, in which functions $I_i^L(\mathbf{q}, \omega)$ have the simple form

$$I_1^L(0,\omega) = g_0^{-2} + \left(\frac{\omega}{2A}\right)^2 N(0)I(\omega) ,$$

$$I_2^L(0,\omega) = -\frac{\omega}{2A} N(0)I(\omega) , \qquad (3.26)$$

$$I_3^L(0,\omega) = N(0)I(\omega) , \qquad \tilde{I}_3^L(0,\omega) = 0 ,$$

where

$$I(\omega) = \frac{2\Delta}{\omega} \begin{cases} \frac{\arcsin\left(\omega/2\Delta\right)}{\sqrt{1 - (\omega/2\Delta)^2}}, & \omega < 2\Delta, \\ \frac{i\pi/2 - \operatorname{arsinh}\sqrt{(\omega/2\Delta)^2 - 1}}{\sqrt{(\omega/2\Delta)^2 - 1}}, & \omega > 2\Delta. \end{cases}$$

$$(3.27)$$

One can see from formulas (3.25) and (3.26) that

$$\Pi_{s,L=0}(\mathbf{q}=0,\omega) = 0.$$
(3.28)

This result presents an important consequence of the Ward identity which is valid in the Fröhlich model, as well as in any system with a gradient-invariant Hamiltonian. The identity only holds true at the proper allowance made for the vertex corrections [35]. It is just that nontrivial consequence of accounting for the vertex corrections mentioned above. The value of phonon self-energy without taking into account the vertex corrections (i.e., at $\Gamma = g$) does not satisfy identity (3.28). As was shown in Refs [32, 38], the isotropic long-range Coulomb interaction related directly to the L = 0 component of the self-energy $\Pi_{s,L=0}(\mathbf{q},\omega)$ turns it to zero at q=0. As we ascertained in systems with a gradient-invariant Hamiltonian, this quantity is zero on its own accord. Hence, phonons with q = 0, possessing the representation with L = 0 (or, from the viewpoint of the crystal group theory, the identical representation with total point-group symmetry), interact with electrons in neither normal, nor superconducting states and possess no nonadiabatic corrections. This fact, in contrast to the assertions in papers [32, 38], arises from the accurate consideration for the vertex corrections even in the absence of the long-range Coulomb interaction. Of course, the allowance made for Coulomb interaction may result, similarly to the case of dielectric response [35-37], in the renormalization of the corresponding polarization operators and characteristic constants, such as N(0). Nevertheless, this circumstance does not change the underlying physics of nonadiabatic effects as long as there are no low-energy collective excitations of the charge density or electron spin.

Consider now the $L \neq 0$ components of the self-energy of phonons that are independent of the long-range isotropic Coulomb interaction:

$$\Pi_L(\mathbf{q},\omega) = -2\lambda_L \frac{I(\omega)}{1 - \lambda_L \beta_L(\omega/2\Delta) I(\omega)}, \qquad (3.29)$$

where $\lambda_L = g_L^2 N(0)$ is the coupling constant in the *L*-channel, and

$$\beta_L \left(\frac{\omega}{2\Delta}\right) = \left(\frac{\omega}{2\Delta}\right)^2 \frac{\lambda_0}{\lambda_0 - \lambda_L} - 1.$$
(3.30)

Expression (3.29) illustrates the possibility of existing a pole in the polarization operator in the $L \neq 0$ channel, which is known in the theory of superconductor electromagnetic response [35]. The corresponding condition is formulated as

$$1 - \lambda_L I(\omega_{\rm b}) \,\beta_L\left(\frac{\omega_{\rm b}}{2\Delta}\right) = 0\,. \tag{3.31}$$

From this expression one can find the energy of collective excitations:

$$\omega_{\rm b} \approx 2\Delta - \Delta \lambda_L^2 \left(\frac{\lambda_L}{\lambda}\right)^2.$$
 (3.32)

It was shown in early work by Maki and Tsuneto [39] that the allowance made for the impurity scattering of electrons may noticeably change the expressions obtained above for the electron response functions. In particular, this may result in the disappearance of the pole in the polarization operator and, consequently, in vanishing the collective electron excitations. This problem was thoroughly discussed in Ref. [40] when studying Raman light scattering spectra in superconductors. That work provided the support for the results obtained in Ref. [39] and it was demonstrated that the vertex corrections may be neglected in the case of strongly disordered systems. These results can be easily generalized to the case of the nonadiabatic effects in phonon spectra of superconductors under discussion. Such a generalization was made for optical phonons with q = 0 in Ref. [41], where the cases of isotropic s-pairing, as well as anisotropic d-pairing, were considered. In that work it was, in particular, shown that in the weak coupling approximation the allowance made for the vertex corrections does not lead to a considerable change in phonon spectral functions, even for impurity-free systems.

Consider now the nonadiabatic corrections for optical phonons with $L \neq 0$ in the simplest approximation without accounting for vertices. For this purpose let us rewrite Eqn (3.3) which defines the renormalization of phonon frequencies:

$$\omega_{sL}^2 = \omega_0^2(0, s, L) \left[1 + \Pi_{sL}(0, \omega_{sL}) \right].$$
(3.33)

In this approximation, the polarization operator takes the form [22]

 $\Pi_{sL}(0,\omega)$

$$= -2\lambda_{sL} \left(\frac{2\Delta}{\omega}\right) \begin{cases} \frac{\arcsin\left(\omega/2\Delta\right)}{\sqrt{1 - \left(\omega/2\Delta\right)^2}}, & \omega < 2\Delta, \\ \frac{i\pi/2 - \operatorname{arsinh}\sqrt{\left(\omega/2\Delta\right)^2 - 1}}{\sqrt{\left(\omega/2\Delta\right)^2 - 1}}, & \omega > 2\Delta. \end{cases}$$

$$(3.34)$$

To begin with, notice that in the framework of the simplest approximations used a number of very nontrivial effects show their worth. First, the phonon linewidth at energies $\omega \leq 2\Delta$ vanishes at T = 0; however, it is distinct from zero in the superconducting state for $T < T_c$. For $\omega \geq 2\Delta$, the linewidth of optical phonons in the superconducting state is nonzero, even at T = 0. The zero linewidth for energies $\omega \leq 2\Delta$ only at first glance is a natural consequence of the presence of a gap in the electron excitation spectrum. One should remember that in a normal state the linewidth of optical phonons is zero at $\mathbf{q} = 0$ for all frequencies. In the superconducting state, the nonzero linewidth at all energies and also at T = 0 when $\omega \ge 2\Delta$ is a consequence of appearing the new channel in EPI and is related to a possible decay of a Cooper pair of electrons.

Second, phonons soften for $\omega \leq 2\Delta$, i.e., their frequencies become lower. Moreover, the polarization operator at low frequencies may be represented in the form

$$\Pi_{sL}(\omega) \approx -2\lambda_{sL} \left[1 + \frac{2}{3} \left(\frac{\omega}{2A} \right)^2 \right].$$
(3.35)

This means that the superconducting system, figuratively speaking, becomes 'more adiabatic' with respect to low-frequency phonons. The renormalization of phonon frequencies and occurrence of phonon attenuation in the superconducting state for $\omega < 2\Delta$ resembles the behavior of underdoped narrow-gap semiconductors.

The expression for the polarization operator, coinciding with Eqn (3.34), was obtained by Zeyher and Zwicknagl [42]. In their later work, the authors, however, subtracted the constant term $-2\lambda_s$ from the polarization operator. The reason for doing so is as follows. In works [32, 42], the EPI constant $\lambda = 2.9$ was utilized. However, Eqns (3.33) and (3.34) have no solutions for $\omega < 2\Delta$ and $\lambda > 1/2$, which, in turn, is a consequence of the instability of bare phonons for $\lambda > 1/2$ [see formulas (3.5) and (3.7)]. The subtraction of the constant term $\Pi_{sL}(0) = -2\lambda_{sL}$ from the polarization operator eliminates this peculiarity of the Fröhlich model. In this case, however, physically clear 'adiabatic' behavior of phonon modes, occurring in a superconducting system for $\omega < 2\Delta$ and obtained by us earlier [see formula (3.35)], vanishes from the solutions to Eqns (3.33), (3.34). We will discuss these problems in the next section of the review.

The frequencies of optical phonons for $\omega_{ph} \ge 2\Delta$, as follows from formulas (3.34), harden as compared to the spectra in a normal state. Magnitudes of the corresponding effects in this case are at their maxima at $\omega_{ph} \approx 2\Delta$. Similar effects were observed in studying phonons in high-temperature superconductors [31, 43].

It should be immediately noted that a number of additional effects show themselves at $\omega_{\rm ph} \approx 2\varDelta$ in the framework of the approximation considered above and that they are more interesting than simple changes in phonon frequencies. Due to the root singularity in the dependence of the polarization operator (3.34) at $\omega = 2\Delta$, two solutions to Eqn (3.33) may exist for the phonon frequency squared. As mentioned above, such a possibility was first predicted by Schuster [11] for acoustic phonons. Nevertheless, no such lines were observed in the spectra of acoustic phonons [10]. Later on, the corresponding behavior of the phonon spectral function was observed in NbSe₂ for a low-frequency optical phonon with $\omega_{\rm ph} \approx 2\Delta$ [12]. Theoretical interpretation of this phenomenon was given in Ref. [44], being close to that suggested by Schuster [11]. The existence of two solutions to Eqn (3.33) can be easily understood by considering the mode with $\omega_0 \ge 2\Delta$. In this case, for the first solution $(\omega_1 \approx \omega_0 \gg 2\varDelta)$ we have

$$\omega_1^2 \approx \omega_0^2 \left(1 + 2\lambda_s \ln \frac{\omega_0}{2\Delta} \right). \tag{3.36}$$

While the second solution ($\omega_2 < 2\Delta$) is given by

$$\omega_2^2 \approx (2\varDelta)^2 (1 - \pi^2 \lambda_L^2) \,. \tag{3.37}$$

Thus, the split mode with energy ω_2 exists for optical phonons possessing arbitrary energy ω_0 , and the frequency of this mode is actually independent of the phonon energy ω_0 . For obtaining more accurate results in this range of phonon energy one should numerically calculate both the energy and intensity of the split mode. Certain results of such calculations will be presented below.

In Refs [11, 44], the nonadiabatic effects in phonon spectra of superconductors were considered using the abovedescribed standard Fröhlich Hamiltonian without direct Coulomb electron-electron interaction. Based on this fact, the results obtained in Ref. [44] were criticized by Littlewood and Varma [38]. They asserted that the allowance made for the long-range Coulomb interaction at small wave vectors results in the complete screening of all contributions (including nonadiabatic) from electron-phonon interactions to the phonon frequencies. To explain the experimentally found phenomena, they invoked the specificity of the low-frequency optical mode in NbSe2, considering it as an amplitude mode of the charge density wave which, according to their hypothesis, exists in the system. It should be noted that this optical mode possesses no particular specificity, being related to a structural transition into an incommensurable phase. This mode is specific, first, in that its frequency is noticeably lower than the frequencies of all other optical phonons in the metal and is close to 2Δ in magnitude. Second, this mode does not possess a total symmetry of the crystal lattice, hence, it is not screened by the Coulomb interaction and the matrix element of its nonadiabatic interaction with electrons is distinct from zero.

The appearance of the new phonon mode with the energy $\omega(\mathbf{q}) \leq 2\Delta$ in the superconducting state may also occur at large wave vectors \mathbf{q} . The phonon spectra of low-energy acoustic and optical branches in superconducting nickel boron carbides YNi₂B₂C and LuNi₂B₂C were studied by application of inelastic neutron scattering [13, 45, 46]. It was found that the frequencies of both branches in the direction $(\xi, 0, 0)$ at wave vectors **q** on the order of the half reciprocal lattice vector ($\xi \approx 0.55$) in a normal state reduced with decreasing temperature, and below the superconducting transition temperature T_c the phonon spectrum changed drastically. A narrow peak arose at the energy of about 4 meV, which is slightly lower than 2Δ , as well as the wide maximum appropriate to the energy of the phonons under study. This effect was explained in Refs [47, 48], where the polarization operator $\Pi_{sL}(\mathbf{q},\omega)$ was calculated for finite **q** in the quasiisotropic approximation. The results of these calculations are very close to those obtained by Schuster [11] and can be confirmed by using formulas (3.22)-(3.25) for momenta $q \neq 0$ meeting the condition

$$k_{\rm F} > q > \frac{\omega}{v_{\rm F}}, \frac{2\Delta}{v_{\rm F}}.$$

$$(3.38)$$

It can be easily shown that functions $I_j^L(\mathbf{q}, \omega)$ reduce in this case to the following expressions

$$\begin{split} \tilde{I}_{3}(\mathbf{q},\omega) &\approx N(0) ,\\ I_{2}(\mathbf{q},\omega) &= -\frac{\omega}{2\Delta} N(0) I_{3}(\mathbf{q},\omega) ,\\ I_{1}(\mathbf{q},\omega) &\approx N(0) I_{3}(\mathbf{q},\omega) . \end{split}$$
(3.39)

From formulas (3.34) and (3.25) it follows that the vertex corrections at large values of phonon momenta **q** do not lead to an origin of the pole in the vertex functions and can be

neglected in the weak coupling approximation considered. The self-energy of the phonon Green function in this case takes the form

$$\Pi_{s}(\mathbf{q},\omega) = -2g_{s}^{2}N(0) - 2g_{s}^{2}N(0) I_{3}(\mathbf{q},\omega), \qquad (3.40)$$

where at energies $\omega \rightarrow 2\Delta$ we have

$$I_{3}(\mathbf{q},\omega) \approx \frac{\pi\omega}{2\mathbf{q}\mathbf{v}_{\mathrm{F}}} \left[\ln \frac{2\varDelta}{|2\varDelta - \omega|} + \mathrm{i}\Theta(\omega - 2\varDelta) \right], \qquad (3.41)$$

which exactly coincides with the result obtained in Refs [11, 47]. One can show [48] that in this case the spectral weight of the split mode and the split magnitude $|2\Delta - \omega(\mathbf{q})|/2\Delta$ comprise exponential smallness of order exp $(-\mathbf{q}\mathbf{v}_{\rm F}/\lambda\Delta) \ll 1$. From the formal point of view, these formulas, as was shown in Ref. [47], can be used to describe the experimental data presented in Refs [13, 45, 46]. Actually, the quasiisotropic model suggested in Refs [47, 48] is not, obviously, appropriate for this purpose because the weak logarithmic singularity in polarization operator (3.41) determines the choice of the parameters needed for describing the case of $T < T_{\rm c}$, which we do not consider realistic.

Theoretical evaluations [49] of the electron polarizability of $LuNi_2B_2C$ compound, in addition to the fact that the frequencies of phonons of both branches with wave vectors on the order of the half reciprocal lattice vector fall at lower temperatures, point to the presence of so-called nesting in the electronic spectrum for sufficiently large sections of the Fermi surface. The term 'nesting' usually means the fulfillment of the relationship

$$\xi_{\mathbf{p}} \approx -\xi_{\mathbf{p}+\mathbf{Q}} \tag{3.42}$$

for single-electron energies in a finite phase volume near the Fermi surface. Vector \mathbf{Q} , for which relationship (3.42) is valid, is called a nesting vector. It is known [50] that under the exact fulfillment of condition (3.42) (the ideal nesting) the static electron polarizability $\chi(\mathbf{q}, 0)$ has a singularity (pole) at the wave vector $\mathbf{q} = \mathbf{Q}$. This fact, in turn, may lead to considerable softening of the phonon modes with wave vectors \mathbf{q} that are close to nesting vector \mathbf{Q} ; in particular, it may result in a structural transition.

By using formulas (3.22)–(3.25) one can find $\Pi_{sL}(\mathbf{Q},\omega)$ for the case of ideal nesting:

$$I_{1}(\mathbf{Q},\omega) \approx N(0)I(\omega), \qquad I_{2}(\mathbf{Q},\omega) = -\frac{\omega}{2\Delta}N(0)I(\omega),$$
$$I_{3}(\mathbf{Q},\omega) = N(0)\ln\left(\frac{2\omega_{c}}{\Delta}\right) + \left(\frac{\omega}{2\Delta}\right)^{2}N(0)I(\omega), \qquad (3.43)$$
$$\tilde{I}_{3}(\mathbf{Q},\omega) = N(0)\ln\left(\frac{\varepsilon_{F}}{\omega_{c}}\right).$$

Correspondingly, for the channel L = 0 at T = 0, assuming for simplicity that $\lambda_{L=0} \approx \lambda \approx \lambda_{\mathbf{Q}}$, one can find for $\Pi_{sL=0}(\mathbf{Q}, \omega \rightarrow 2\Delta)$ the following expression:

$$\Pi_{sL}(\mathbf{Q},\omega) = -2\lambda_{\mathbf{Q}} \ln\left(\frac{\varepsilon_{\mathrm{F}}}{\varDelta}\right) - 2\lambda_{\mathbf{Q}} \frac{1/\lambda - I(\omega)}{2 - \lambda_{\mathbf{Q}}I(\omega)}.$$
 (3.44)

Here, $\lambda_{\mathbf{Q}} = g^2(\mathbf{Q})N(0)$, and λ is the total electron – phonon coupling constant determined by the condition

$$1 = \lambda \ln \left(\frac{2\omega_{\rm c}}{\Delta}\right). \tag{3.45}$$

The first summand in expression (3.44) is well known [50, 51] and describes the cancellation of singularity of static response functions in the systems experiencing nesting, when the system transfers to a superconducting state. In a normal state, this term equals $-2\lambda_0 \ln (\varepsilon_F / \max \{\omega, T\})$. This circumstance, in particular, stops the softening of phonon modes in the adiabatic approximation and leads to the absence of structural transformations for $T < T_c$. The second summand describes the singular behavior of function $\Pi_{sL}(\mathbf{Q},\omega)$ at the energies $\omega \approx 2\Delta$ and is just connected with a transition to a superconducting state. It can be inferred from formula (3.44) that $\Pi_s(\mathbf{Q}, \omega)$, similarly to the case of q = 0, has a pole responsible for collective excitations. By comparing the expressions (3.44) and (3.29) for the polarization operator in zero approximation one can see that $\Pi_{sL}(\mathbf{Q},\omega)$ in the case of nesting at $\omega \approx 2\Delta$ has just the same singularity as at q = 0, namely, $\sim 1/[1 - (\omega/2\Delta)^2]^{1/2}$, but already in the isotropic channel with L = 0.

Inasmuch as ideal nesting in real physical systems is hardly probable, in our work [22] on more thorough modeling of the experiment we made numerical calculations of Im $D_s(\mathbf{q}, \omega)$ by employing the model in which nesting varies from the ideal case to an absolute absence. We applied the two-dimensional model of a square lattice of strongly bound electrons with nearest-neighbor overlapping. The electronic spectrum of such a system can be represented in the form

$$\xi_{\mathbf{p}} = -2t(\cos p_x + \cos p_y) - \mu \,,$$

where μ is the chemical potential of the system that characterizes the degree of band filling, and t is the overlap integral. If the band is half-filled ($\mu = 0$), the Fermi surface is a square, which means that the system is characterized by ideal nesting. At poor filling, the Fermi surface is close to a circle, which corresponds to a standard quasiisotropic system. By varying the degree of band filling one can study the whole transition range from ideal nesting to an isotropic system. Earlier, this model was used in Ref. [52] for calculating the self-energy of phonon Green functions in superconductors. However, the phonon Green functions themselves and the corresponding spectral densities Im $D_s(\mathbf{q}, \omega)$ were not calculated in that work. We made numerical calculations of function Im $D_s(\mathbf{q}, \omega)$ in the framework of the model with isotropic pairing by making complete allowance for the vertex corrections. Two phonon modes $\omega^{(1)}(\mathbf{q})$ and $\omega^{(2)}(\mathbf{q})$ with different coupling constants were considered as functions of temperature. It was assumed that the bare frequencies for these modes (without EPI) are degenerate, i.e., $\omega_0^{(1)}(\mathbf{q},s) = \omega_0^{(2)}(\mathbf{q},s) = 250$ K. The electron-phonon coupling constants for these modes were chosen as $\lambda_1 = 0.1$ and $\lambda_2 = 0.085$, respectively, so that $\lambda_1 > \lambda_2$. The total coupling constant $\lambda = 0.372$ was determined from condition (3.32) in such a way that $\Delta \approx 3 \text{ meV}$ at $\omega_c \approx 3 \text{ meV}$. Such a choice of Δ and ω_{c} approximately corresponds to the values observed in boron carbides. In Fig. 2, the calculated intensity is shown for phonon modes $\omega^{(1,2)}(\mathbf{q})$ with the quasinesting vector \mathbf{q} joining the sections of the Fermi surface possessing close curvatures for the band fillings 1.11 and 0.89 electrons per center $(\mu = \pm 0.2)$ and temperatures $T = T_c$ and T = 0. The theoretical curves in Fig. 2 qualitatively agree with the experimental data taken from Refs [13, 45, 46]. In this figure, one can clearly see an additional narrow mode with the energy below 2 Δ , which appears for $T < T_c$. The sharp broadening of phonon lines at energies greater than 2Δ , occurring in the



Figure 2. The intensities of two phonon lines at T = 0 (solid curve) and for $T > T_c$ (dashed line). The calculations were performed in the Fröhlich model.



Figure 3. Calculated temperature dependences of the energy (solid curve) and intensity (squares) of a split phonon mode in the superconducting state.

superconducting state, can also be evidenced. The intensities of these lines are appreciably transferred to the additional mode. The closer the mode energy to 2Δ , the more noticeable this transfer (the intensity is more noticeably transferred from softer mode 1 than from mode 2).

Let us briefly dwell on the temperature dependences of the characteristics of the phonon mode which is observed in the superconducting state below 2Δ . In the framework of the BCS model considered above, the temperature dependences of the energy and intensity of this mode are determined by the dependence of the parameter 2Δ on temperature. The experimental data from Refs [13, 45, 46] show a distinct deviation from such a behavior. The energy of the additional mode is actually independent of temperature, whereas its intensity is reduced with increasing temperature much faster than the parameter 2Δ does. This fact can be naturally explained in the framework of the strong coupling theory based on Eliashberg equations [33]. The fact is that due to EPI the lifetime of electrons becomes finite, even in a superconducting state and depends on energy and temperature. In addition, EPI removes singularities from the response functions and from the density of electron states [53]. The relaxation time of electrons rises drastically as $T_{\rm c}$ is approached, which leads to an abrupt fall in the intensity of the additional mode. It is natural that in the framework of the

strong coupling theory the mode energy noticeably falls as T tends to T_c . However, this occurs in the temperature range in which the mode intensity is small and cannot actually be observed. The results of numerical calculations for the energy of the split mode and its intensity are depicted in Fig. 3. They definitely confirm the qualitative explanation given above.

4. Microscopic theory of lattice dynamics

To answer the question whether the Fröhlich Hamiltonian has a physical meaning and what the adiabatic phonons and nonadiabatic corrections are in essence, it is necessary to revert to the exact microscopic theory of lattice dynamics, since in the framework of the adiabatic approximation it is difficult to apply the standard methods of many-body theory.

In the framework of the standard many-particle perturbation theory for the electron-ion Hamiltonian, the exact equations for single-particle Green functions of electrons and phonons have been obtained [23]. The phonon contribution to the electron excitation spectrum formally has the same form as the nonadiabatic corrections to the electron energy in the framework of the adiabatic approach [see formula (2.15)]. We get just the same answer in the framework of the Fröhlich model. Problems arise in making consistent microscopic calculations of the EPI matrix element. In this calculation one should take into account the vertex corrections arising due to Coulomb interelectron interaction, in addition to the screening of the electron potential gradient. There is one more difference between the results of electron spectrum renormalization, which were obtained in the adiabatic approach (2.15) and in the microscopic lattice theory. It is mainly related to the differences in the mathematical apparatus utilized in these approaches. In the microscopic approach, the Green function technique is used and the self-energy is calculated for the single-particle electron Green function. One can show that, similarly to the Fröhlich model, the self-energy is independent of the electron momentum **p**, but depends on energy ω , which is connected with the retarded character of EPI. This fact is rather important in describing many properties of an electron subsystem in crystals, in particular, the photoemission spectra [54]. The Green function for an electron is given in the form

$$G^{-1}(\mathbf{p},\omega) = \omega - \xi_{\mathbf{p}} - \Xi(\omega), \qquad (4.1)$$

where $\Xi(\omega)$ is the self-energy [58]. At zero temperature and low energies, $\Xi(\omega)$ may be written out in the simple form

$$\Xi(\omega) = \lambda \omega \,, \tag{4.2}$$

where λ is the electron – phonon coupling constant. From the condition $G^{-1}(\mathbf{q}, \omega) = 0$, one can calculate the spectrum of electron excitations and it will coincide with the results obtained in the adiabatic approach. In the framework of the density functional theory, an efficient method was developed [55] for calculating EPI matrix elements and their subsequent employment in the Fröhlich model for determining the electron properties of normal and superconducting metal states. In particular, the EPI constant may be calculated. A description of this method is beyond our review.

It was also shown [23] that the single-particle Green function for phonons in the harmonic approximation is governed by just the same equation as in the adiabatic approximation; however, the electron contribution to the dynamic vibrational matrix is made by the frequencydependent electron susceptibility. This means that in Eqns (2.10) and (2.11) for matrix $\overline{\Phi}^{\alpha\beta}(\mathbf{q})$ we must replace the matrix of static susceptibility $\chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega = 0)$ by matrix $\chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega)$. In such a multiparticle approach, the nonadiabatic corrections to phonon spectra of metals arise for the following reasons. First, because of the frequency dependence of the electron susceptibility matrix; second, because this susceptibility should now be calculated with allowance made for EPI rather than for a stationary lattice, as it is in the adiabatic approximation. This means that in calculating the electron loops one should rely on single-electron Green functions which make allowance for the EPI contribution. Whenever essential, it is necessary to take into account the contributions from the electron – phonon interaction to vertex functions, as well.

As was already mentioned, the exact quantitative calculations for the infinite-dimensional matrix of electron susceptibility are beyond our computation possibilities. In the theory of the density functional, direct methods are used for calculating the variations in electron density under static ion displacements. This makes it possible to find forces acting on ions and, correspondingly, calculate the dynamic matrix of vibrations (see reviews [25, 26]). Unfortunately, such ab initio methods for calculating nonadiabatic effects are not developed yet. For this purpose, at least, the method of density functional should be generalized in such a way that it would be the functional not only of electron density but of ion density as well. Nevertheless, it is possible to answer many principal questions related to nonadiabatic effects in the phonon spectra of metals by using the general expressions for the dynamic vibrational matrix presented in Section 2.

We may write the electron contribution to the matrix of vibrations in the form of two summands by using the method suggested by Allen [56]. For simplicity, this procedure can be presented in a symbolic form by writing out the electron susceptibility as

$$\chi = \Pi \varepsilon^{-1} \,, \tag{4.3}$$

where Π is the polarization operator. Now we may multiply the left-hand side of this equality by $1 = \tilde{\epsilon}^{-1}\tilde{\epsilon}$, where $\tilde{\epsilon}$ is the transposed matrix of electron dielectric function. Then we arrive at

$$\chi = \tilde{\varepsilon}^{-1} (1 - \Pi V_{\rm c}) \, \Pi \varepsilon^{-1} = \tilde{\varepsilon}^{-1} \Pi \varepsilon^{-1} - \tilde{\chi} V_{\rm c} \, \chi \,. \tag{4.4}$$

Here, V_c is the matrix element for the Coulomb electron – electron interaction. The electron contribution to the matrix of force constants $C_{nn'}^{\alpha\beta}$ can be written in the form

$$C_{nn'}^{\alpha\beta} = \int d\mathbf{r} \, d\mathbf{r}' \, \nabla_{\alpha} \tilde{V}_{ei}(\mathbf{r} - \mathbf{R}_n) \, \Pi(\mathbf{r}, \mathbf{r}', \omega) \, \nabla_{\beta} \tilde{V}_{ei}(\mathbf{r}' - \mathbf{R}_{n'}) - \int d\mathbf{r} \, d\mathbf{r}' \, \delta\rho_{\alpha}(\mathbf{r} - \mathbf{R}_n) \, V_{c}(\mathbf{r} - \mathbf{r}') \, \delta\rho_{\beta}(\mathbf{r}' - \mathbf{R}_{n'}) \,. \quad (4.5)$$

We introduced the following notations for the screened electron interaction potential $\nabla_{\alpha} \tilde{V}_{ei}(\mathbf{r} - \mathbf{R}_n)$ and the variation $\delta \rho_{\alpha}(\mathbf{r} - \mathbf{R}_n)$ of electron charge density:

$$\nabla_{\alpha} \tilde{V}_{ei}(\mathbf{r} - \mathbf{R}) = \int d\mathbf{r}' \, \nabla_{\alpha} V_{ei}(\mathbf{r}' - \mathbf{R}_n) \, \tilde{\varepsilon}^{-1}(\mathbf{r}, \mathbf{r}', \omega) \,, \quad (4.6)$$

$$\delta \rho_{\alpha}(\mathbf{r} - \mathbf{R}_n) = \int d\mathbf{r}' \, \nabla_{\alpha} V_{\text{ei}}(\mathbf{r}' - \mathbf{R}_n) \, \tilde{\chi}(\mathbf{r}, \mathbf{r}', \omega) \,. \tag{4.7}$$

The second summand in expression (4.5) is the Coulomb interaction of distributed electron charges. One can exactly

show [56], and we will do so later on in the simplest approximation for electron response matrices, that this summand yields, along with the ion contribution in metals, the 'correct' metal behavior for phonon frequencies. This means that the longitudinal acoustic modes, with the ion contribution and second summand in expression (4.5) taken into account, are of acoustic character and the longitudinal and transverse optical modes are not split. The allowance made for these summands in itself does not result in exact phonon frequencies in metal since the first summand in expression (4.5) contributes to the dispersion of phonons as well and this contribution is not small. Let us consider the first summand in expression (4.5) more thoroughly. It resembles the contribution that arises from the electron-phonon interaction in the Fröhlich model. We will show that it is precisely from this contribution that the main nonadiabatic corrections to phonon frequencies come. It is natural that it makes, as was mentioned, a nonzero contribution to the phonon dispersion, as well. From this point of view, the separation of the electron contribution into the dynamic matrix of vibrations can be considered, in some sense, as a 'ground' for the Fröhlich model in which the bare phonon frequencies arise due to ion-ion interaction and the second summand in formula (4.5). Literally, as we will see below, the Fröhlich model cannot be completely substantiated in the framework of the microscopic theory.

Let us now consider the simplest approximation for metal, assuming its electrons are free particles. Such an approach was fruitful in describing the lattice dynamics of simple metals (see review [16]). Its employment was substantiated by a low electron-ion pseudopotential as compared to the direct Coulomb electron-ion interaction. In the first approximation in this small pseudopotential, the electron response matrix can be written out in the form

$$\varepsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) = \delta_{\mathbf{G}, \mathbf{G}'} \varepsilon(\mathbf{q} + \mathbf{G}, \omega), \qquad (4.8)$$

where $\varepsilon(\mathbf{q}, \omega)$ is the dielectric function of free electron gas with the Coulomb electron–electron interaction taken into account, however. The electron contribution to the dynamic vibrational matrix (4.5) can be written in the form

$$\begin{split} \Phi^{\alpha\beta}(\mathbf{q}) &= \frac{1}{\Omega_0} \sum_{\mathbf{G}} \frac{(\mathbf{q} + \mathbf{G})^{\alpha} V_{\mathrm{ei}}(\mathbf{q} + \mathbf{G})}{\varepsilon(\mathbf{q} + \mathbf{G}, \omega)} \Pi(\mathbf{q} + \mathbf{G}, \omega) \\ &\times \frac{(\mathbf{q} + \mathbf{G})^{\beta} V_{\mathrm{ei}}(\mathbf{q} + \mathbf{G}, \omega)}{\varepsilon(\mathbf{q} + \mathbf{G}, \omega)} \\ &- \frac{1}{\Omega_0} \sum_{\mathbf{G}} (\mathbf{q} + \mathbf{G})^{\alpha} V_{\mathrm{ei}}(\mathbf{q} + \mathbf{G}) \frac{\Pi(\mathbf{q} + \mathbf{G}, \omega)}{\varepsilon(\mathbf{q} + \mathbf{G}, \omega)} \frac{4\pi e^2}{(\mathbf{q} + \mathbf{G})^2} \\ &\times \frac{\Pi(\mathbf{q} + \mathbf{G}, \omega)}{\varepsilon(\mathbf{q} + \mathbf{G}, \omega)} (\mathbf{q} + \mathbf{G})^{\beta} V_{\mathrm{ei}}(\mathbf{q} + \mathbf{G}) \,. \end{split}$$
(4.9)

We wrote expression (4.9) for the case of a crystal with a single atom per unit cell to simplify the formula. Notice that for $\mathbf{G} \neq 0$ we may neglect the dependence of functions $\varepsilon(\mathbf{q} + \mathbf{G}, \omega)$ and $\Pi(\mathbf{q} + \mathbf{G}, \omega)$ on ω , since $\mathbf{G}\mathbf{v}_F \gg \omega$. Consider the second summand with $\mathbf{G} = 0$ in more detail:

$$-\frac{1}{\Omega_0} q^{\alpha} V_{\rm ei}(\mathbf{q}) \frac{\Pi(\mathbf{q},\omega)}{\varepsilon(\mathbf{q},\omega)} \frac{4\pi e^2}{\mathbf{q}^2} \frac{\Pi(\mathbf{q},\omega)}{\varepsilon(\mathbf{q},\omega)} q^{\beta} V_{\rm ei}(\mathbf{q}).$$
(4.10)

By writing $\varepsilon(\mathbf{q}, \omega)$ in the form

$$\varepsilon(\mathbf{q},\omega) = 1 - \frac{4\pi e^2}{\mathbf{q}^2} \Pi(\mathbf{q},\omega), \qquad (4.11)$$

one can easily see that the dependence on ω completely vanishes in expression (4.10) as $q \rightarrow 0$, so that instead of formula (4.10) we obtain

$$-\frac{4\pi e^2 Z^2}{\Omega_0} \frac{q^{\alpha} q^{\beta}}{q^2} \,. \tag{4.12}$$

In deriving this formula we retained in the electron pseudopotential at small **q** its most substantial part only, i.e., the Coulomb contribution $V_{\rm ei}(\mathbf{q}) \approx 4\pi e^2 Z^2/q^2$. It is easy to verify that the electron contribution (4.12) to the dynamic matrix of vibrations completely compensates for the same contribution from the ion vibrations in the acoustic longitudinal mode, thus transforming this plasma mode into an acoustic one. In the case of optical vibrations, this contribution completely compensates for the splitting of the longitudinal and transverse modes, present in an ion contribution, and we thus obtain

$$\omega_{\rm LO}^2(\mathbf{q}=0) = \omega_{\rm TO}^2(\mathbf{q}=0).$$
(4.13)

Therefore, we have shown that the second summand in expression (4.9), along with the ion contribution, gives rise to a crystal spectrum of the metal type. This summand comprises no nonadiabatic corrections except for those small with respect to $\sqrt{m/M}$, at least in the approximation of free electrons.

Consider now the first summand in expression (4.9). It is easy to verify that in the adiabatic approximation, i.e., neglecting the dependence of the response function on frequency ω , this summand contributes only to the dispersion of acoustic and optical modes. This contribution, at least to the longitudinal modes, is not small. Then, for the frequency of the longitudinal optical mode we obtain the following expression as $\mathbf{q} \rightarrow 0$:

$$\omega_{\rm LO}^2 = \omega_{\rm TO}^2 + \frac{4\pi e^2 Z_1 Z_2}{\Omega_0 \tilde{M}} \frac{1}{\varepsilon(\mathbf{q}, \omega)} \,. \tag{4.14}$$

Here, \tilde{M} is the reduced ion mass in the lattice. In the adiabatic approximation, the second summand in expression (4.14) vanishes as $\mathbf{q} \to 0$, whereas in the nonadiabatic limit we have

$$\omega_{\rm LO}^2 = \omega_{\rm TO}^2 - \frac{4\pi e^2 Z_1 Z_2}{\Omega_0 \tilde{M}} \frac{\omega_{\rm LO}^2}{\omega_{\rm pl}^2} , \qquad (4.15)$$

where ω_{pl} is the electron plasma frequency:

$$\omega_{\rm pl}^2 = \frac{4\pi n e^2}{m} \,. \tag{4.16}$$

From expressions (4.15) and (4.16) it follows that in the nonadiabatic limit the longitudinal and transverse modes split. The longitudinal mode frequency becomes lower than that of the transverse one — that is, the antiscreening of longitudinal modes arises. The magnitude of this splitting in the free electron approximation is small to the extent of smallness of the parameter $\sqrt{m/M}$. Of course, one can calculate the linewidth of phonon modes determined by the nonadiabatic effects, but from the above consideration it is evident that in a metal in the approximation of free electrons no nonadiabatic effects arise that lack the smallness of order $\sqrt{m/M}$.

True nonadiabatic effects in both phonon frequencies and their dispersions for $\mathbf{qv}_{\mathrm{F}} \leq \omega_{\mathrm{ph}}$ are contained in off-diagonal matrix elements of the electron response functions. In metals that can be described by means of the weak electron–ion pseudopotential, the off-diagonal matrix elements are small to the extent of smallness of the ratio $V_{\mathrm{ei}}(\mathbf{G})/\varepsilon_{\mathrm{F}}$, where ε_{F} is the Fermi energy. The method for calculating off-diagonal elements by expanding in series of the small parameter $V_{\mathrm{ei}}(\mathbf{G})/\varepsilon_{\mathrm{F}}$ was suggested in Ref. [57]. The greatest nonadiabatic effects arise from the first summand in formula (4.5), which can be written in the form

$$\Phi^{\alpha\beta}(\mathbf{q}) = \frac{1}{\Omega_0} \sum_{\mathbf{G}\neq\mathbf{G}'} \frac{(\mathbf{q}+\mathbf{G})^{\alpha} V_{\mathrm{ei}}(\mathbf{q}+\mathbf{G})}{\varepsilon(\mathbf{q}+\mathbf{G},\omega)} \Pi(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)$$
$$\times \frac{(\mathbf{q}+\mathbf{G}')^{\beta} V_{\mathrm{ei}}(\mathbf{q}+\mathbf{G}')}{\varepsilon(\mathbf{q}+\mathbf{G}',\omega)} . \tag{4.17}$$

In writing down this expression we neglected the off-diagonal matrix elements in the matrix of the inverse dielectric function $\varepsilon^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega)$, because they lead to nonadiabatic corrections which contain higher-order smallnesses with respect to pseudopotential as compared to those taken into account in formula (4.17). It is natural to neglect the dependence of permittivity $\varepsilon(\mathbf{q} + \mathbf{G}, \omega)$ on ω . The off-diagonal matrix element of the polarization matrix $\Pi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega)$, according to Ref. [57], can be written in the form

$$\Pi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) = \frac{V_{ei}(\mathbf{G}' - \mathbf{G})}{\varepsilon(\mathbf{G}' - \mathbf{G}, 0)} \Lambda^{3}(\omega, \mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') + \sum_{\mathbf{G}_{1}, \mathbf{G}_{2}} \frac{V_{ei}(\mathbf{G}_{1})}{\varepsilon(\mathbf{G}_{1}, 0)} \frac{V_{ei}(\mathbf{G}_{2})}{\varepsilon(\mathbf{G}_{2}, 0)} \Lambda^{4}(\omega, \mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \mathbf{G}_{1}, \mathbf{G}_{2}).$$

$$(4.18)$$

The notation introduced in these equations, namely

$$\Lambda^{3}(\omega, \mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}')$$
 and $\Lambda^{4}(\omega, \mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \mathbf{G}_{1}, \mathbf{G}_{2})$

refers essentially to those 'multitails' that were thoroughly studied by Brovman and Kagan [15, 16] in the adiabatic approximation (i.e., at $\omega = 0$). The four-tail term $\Lambda^4(\omega, \mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \mathbf{G}_1, \mathbf{G}_2)$ comprises the delta function of momenta, so that

$$\mathbf{G} + \mathbf{G}' + \mathbf{G}_1 + \mathbf{G}_2 = 0.$$
 (4.19)

We do not write down here the cumbersome expressions for 'multitails' Λ^3 and Λ^4 , but emphasize that no strong nonadiabatic effects are contained in Λ^3 , whereas the second summand in formula (4.17) comprises the nonadiabatic contribution connected with the terms under the sum sign for $\mathbf{G}_1 = -\mathbf{G}$ and $\mathbf{G}_2 = -\mathbf{G}'$. For small \mathbf{q} , the term $\Pi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega)$ can be written in the form

$$\Pi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) = \frac{V_{ei}(\mathbf{G})}{\varepsilon(\mathbf{G}, 0)} \frac{V_{ei}(\mathbf{G}')}{\varepsilon(\mathbf{G}', 0)}$$
$$\times \sum_{\mathbf{p}} \frac{n_{\mathbf{p}+\mathbf{q}} - n_{\mathbf{p}}}{\omega - \xi_{\mathbf{p}+\mathbf{q}} + \xi_{\mathbf{p}} - \mathrm{i}\delta} \frac{2}{(\xi_{\mathbf{p}} - \xi_{\mathbf{p}+\mathbf{G}})(\xi_{\mathbf{p}} - \xi_{\mathbf{p}+\mathbf{G}'})} . \quad (4.20)$$

For a two-atomic crystal along the high-symmetry direction, the contribution of dynamic matrix (4.14) to the frequency of the optical phonon can be written down, in view of formula (4.20), in the form

$$\Delta \omega_{\alpha}^{2}(\mathbf{q} \to 0) = \frac{1}{\Omega_{0}M} \sum_{\mathbf{G},\mathbf{G}',\mathbf{p}} G^{\alpha} G'^{\beta} \frac{V_{\mathrm{ei}}^{2}(\mathbf{G})}{\varepsilon^{2}(\mathbf{G})} \frac{V_{\mathrm{ei}}^{2}(\mathbf{G}')}{\varepsilon^{2}(\mathbf{G}')}$$
$$\times \frac{n_{\mathbf{p}+\mathbf{q}} - n_{\mathbf{p}}}{\omega - \mathbf{q}\mathbf{v}_{\mathrm{F}}} \frac{2\sin\left(\mathbf{G}\right)\sin\left(\mathbf{G}'\right)}{(\xi_{\mathbf{p}} - \xi_{\mathbf{p}+\mathbf{G}})(\xi_{\mathbf{p}} - \xi_{\mathbf{p}+\mathbf{G}'})}, \qquad (4.21)$$

where **l** is the vector connecting two nearest atoms in a unit cell. This expression can be rewritten in a more convenient form

$$\Delta \omega_{\alpha}^{2}(\mathbf{q} \to 0) = \frac{1}{M} \sum_{\mathbf{p}} (V_{\mathbf{p}}^{\alpha})^{2} \frac{n_{\mathbf{p}+\mathbf{q}} - n_{\mathbf{p}}}{\omega - \mathbf{q}\mathbf{v}_{\mathrm{F}}}, \qquad (4.22)$$

where

$$V_{\mathbf{p}}^{\alpha} = \frac{1}{\Omega_0} \sum_{\mathbf{G}} G^{\alpha} \frac{2V_{\mathrm{ei}}^2(\mathbf{G}) \sin \mathbf{G} \mathbf{I}}{\varepsilon^2(\mathbf{G})(\xi_{\mathbf{p}+\mathbf{G}} - \xi_{\mathbf{p}})} \,. \tag{4.23}$$

These results, however, with a slightly distinct approach to the calculation of 'multitails', were obtained over 30 years ago by Ipatova and Subashiev [29]. Formula (4.22) demonstrates that the electron contribution to the phonon frequencies in the microscopic approach comprises the summand which formally exactly corresponds to that in the Fröhlich model. The contribution of this summand to both the adiabatic phonon frequencies for $qv_F \ge \omega_{ph}$ and nonadiabatic effects for $qv_{\rm F} < \omega_{\rm ph}$ contains a fourth-order smallness with respect to pseudopotential. Notice that the adiabatic contributions to optical frequencies from other electron summands yield the second-order smallnesses in powers of pseudopotential. Nevertheless, the nonadiabatic corrections, though having fourth-order smallnesses in powers of pseudopotential, are not small with respect to the nonadiabaticity parameter. It should also be noted that the parameter $V_{\rm ei}(\mathbf{G})/\varepsilon_{\rm F}$ is not small for polyvalent and especially for transition metals. There is one more essential circumstance which follows from formula (4.21), namely, that the nonadiabatic corrections arise due to umklapp processes (i.e., when G and G' are nonzero). Hence, they act similarly on both longitudinal and transverse modes. The only summand differing in its action on longitudinal and transverse optical modes arises from the diagonal summands with $\mathbf{G} = \mathbf{G}' = 0$. It eliminates the splitting of longitudinal and transverse modes, which occurs in the ion contribution in the adiabatic approximation and only results, as was shown in the foregoing [see formula (4.15)], in a weak antiscreening of the longitudinal optical mode.

Summarizing the above results, we may assert that the nonadiabatic effects in spectra of optical phonons, predicted in the framework of the Fröhlich model, may be obtained in both the adiabatic approximation and the microscopic theory of lattice dynamics. Surely, the particular magnitudes of these effects obtained in the framework of the Fröhlich model should be used with caution. One should remember that electronic and phonon spectra are renormalized due to EPI with different coupling constants. A similar situation takes place in the simplest case of the Fröhlich model, in which the self-energy is $\Xi(\omega) = -\omega \lambda_{el}$ [58], where

$$\lambda_{\rm el} = g^2 N(0) \int_0^{2k_{\rm F}} \frac{q \, \mathrm{d}q}{2k_{\rm F}^2} D(q, \omega = 0)$$

= $\lambda \int_0^{2k_{\rm F}} \frac{q \, \mathrm{d}q}{2k_{\rm F}^2} \frac{\omega_0^2}{\omega^2(q)} = \frac{\lambda}{1 - 2\lambda}.$ (4.24)

As was mentioned previously, the coupling constant in papers [32, 42] was chosen as $\lambda_{el} = 2.9$. Such a large value of λ_{el} was used for obtaining $T_c = 91$ K in the YBa₂Cu₃O₇ compound. Renormalization of the electronic spectrum and the critical temperature of superconducting transition are determined just by λ_{el} . From formula (4.24) it follows that in this case the phonon spectrum renormalization constant is as low as 0.4. Hence, no problem must have been arisen in solving Eqns (3.33), (3.34) in Refs [32, 42], if one consistently applied the Fröhlich model.

The real difference in the coupling constants that renormalize the electronic and phonon spectra is not only related to the employment of renormalized phonons in calculating the electronic spectra, as it occurs in the case of the Fröhlich model. It is also related to a substantial difference in the matrix elements of EPI, which determine the renormalization of both the spectra. This can be clearly seen in metals with a weak pseudopotential. Renormalization of electronic spectra in such metals will contain a secondorder smallness with respect to $V_{\rm ei}(\mathbf{G})/\varepsilon_{\rm F}$, whereas the nonadiabatic renormalizations of phonon spectra will have a fourth-order smallness. This circumstance, in particular, makes it possible to understand why the nonadiabatic dispersion of phonons for $qv_F \leq \omega_{ph}$, observed in Refs [6– 8], has a magnitude of the order of $d\omega/dq \approx 10^6$ cm s⁻¹, although the Fermi velocity in osmium is $v_{\rm F} \sim$ $(3-5) \times 10^7$ cm s⁻¹ — that is, the dispersion of phonons is lower than the Fermi velocity by an order of magnitude. Keep in mind that the speed of sound in osmium reaches $\approx 10^4~{\rm cm~s^{-1}},$ i.e., two orders of magnitude lower than the dispersion of optical phonons for $qv_F < \omega_{ph}$. This only means that the coupling constant describing the nonadiabatic effects is $\lambda \simeq 0.1$, although the EPI constant renormalizing the electronic spectrum in osmium is $\lambda_{el} = 0.4$.

It should be noted that in the Fröhlich model, as in the microscopic theory of lattice dynamics, an electron contribution to phonon frequencies exists [see formula (4.22)], which is efficient for both adiabatic and nonadiabatic processes. Hence, in our point of view there is little sense in enhancing the Fröhlich model by various empirical rules, for example, by using $\Pi(\mathbf{q}, \omega) - \Pi(\mathbf{q}, 0)$ instead of the polarization operator $\Pi(\mathbf{q}, \omega)$ in calculating the phonon spectra [17, 20]. Such a procedure does eliminate the renormalization of bare phonon frequencies in the adiabatic limit, however, it would not result in the nonadiabatic effects for optical phonons for $qv_F < \omega_{ph}$ vanishing. In addition, this procedure produces serious problems in considering the nonadiabatic effects in the superconducting state of a metal. The Fröhlich model cannot be corrected by minor updates without losing the sensible physical basis which is contained in it and which agrees with the microscopic theory.

Concluding this section, we would like to briefly answer the criticism against both the idea concerning the existence of nonadiabatic effects in phonon spectra of metals and our work in this field. This criticism is more pronounced in the work by Falkovsky [19, 20, 59], in which it is asserted that the idea itself is wrong on the existence of nonadiabatic effects that are not small quantities with respect to the ratio $\sqrt{m/M}$, and, consequently, that most works concerning these effects are wrong. So, in discussing the experimental data obtained by Ponosov et al. [6–8] it is asserted [19, 20, 59] that the dispersion of an optical phonon in osmium, observed in Refs [6–8], does not prove the existence of nonadiabatic effects in this metal. This conclusion is made on the grounds that the dispersion is lower than the Fermi velocity by a factor of 10. In so doing, the author of papers [19, 20, 59] ignores the fact that the dispersion mentioned is 100 times as great as the speed of sound and the standard dispersion of optical phonons, and that there is no other possibility for explaining such a great difference without invoking nonadiabatic effects. In Ref. [59], formulas for the phonon frequency of the transverse optical mode are presented for the cases of $\mathbf{qv}_{\rm F} < \omega_{\mathbf{q}}$ and $\mathbf{qv}_{\rm F} > \omega_{\mathbf{q}}$, which we rewrite (see formulas (35), (36) in [59]) as

$$\omega_{\rm TO}^2 - i\omega_{\rm TO}^2 \Gamma = \omega_{\bf q}^2 + \lambda \omega_0^2 \frac{\omega_{\bf q}}{\omega_{\bf q} + i\gamma} \qquad (\mathbf{q}\mathbf{v}_{\rm F} < \omega_{\bf q}) \quad (4.25)$$

and

$$\omega_{\rm TO}^2 - i\omega_{\rm TO}^2 \Gamma = \omega_{\bf q}^2 + \lambda \omega_0^2 \left(\frac{\omega_{\bf q}}{\mathbf{q}\mathbf{v}_{\rm F}}\right)^2 \quad (\mathbf{q}\mathbf{v}_{\rm F} > \omega_{\bf q}) \,. \tag{4.26}$$

Here, $\omega_{\mathbf{q}}$ is the bare phonon spectrum, which in Ref. [59] is considered adiabatic, and $\omega_{\mathbf{q}}^2 = \omega_0^2 \pm s^2 q^2$, where *s* is the speed of sound, and λ is the electron-phonon coupling constant. One can clearly see that these formulas for a TO-phonon not only fail to disprove the results of Refs [4, 6– 9, 29, 30] criticized in paper [59], but also completely coincide with the results obtained earlier in the Fröhlich model with slightly different notations. So, the difference between the nonadiabatic frequency squared for the TO-phonon and the adiabatic one, in accordance with formulas (4.25) and (4.26), amounts to $\lambda \omega_0^2$. This is not surprising, since the approach utilized in Refs [19, 20, 59] appreciably coincides with the Fröhlich model, at least for TO-phonons.

5. Conclusion

Let us briefly formulate the results of the discussion presented in this review. First, nonadiabatic effects in the phonon spectra of metals undoubtedly exist and are examined experimentally. They arise due to EPI and are not small with respect to the parameter $\sqrt{m/M}$. In addition to the simplest effects, such as the shift of optical phonon frequencies and increase or reduction of the corresponding widths of phonon lines, they may also lead to more noticeable changes in phonon spectra. Those are the anomalously large dispersion of phonons that arise for $qv_F < \omega_{ph}$, which is a few orders of magnitude greater than the corresponding speed of sound, and additional phonon lines arising in the superconducting state at $\omega_{\rm ph} \approx 2\Delta$. Second, it was shown that such effects occur in both the Fröhlich model and microscopic theory of lattice dynamics. By comparing these two approaches to the calculation of nonadiabatic effects one may conclude that the Fröhlich model can be used for describing the nonadiabatic effects in metals, and the influence of EPI on the properties of an electron subsystem in a metal therewith can be calculated with a high quantitative accuracy. In evaluating the nonadiabatic effects for the phonon spectra of metals the Fröhlich model yields only a qualitative, albeit a physically rational, description of these effects.

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