Long-wave optical-phonon spectrum in metals and heavily doped semiconductors

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The effect of the electron-phonon interaction on the long-wave optical-phonon spectrum in metals and heavily doped semiconductors is considered. It is shown that in the region of phonon momenta $q v_F < \hbar\omega_0$ the electrons lead to a large (not proportional to $\hbar\omega_0/E_F$) nonadiabatic renormalization of the optical-phonon frequency and to strong dispersion of the optical branch. For sufficiently symmetric crystals (e.g., with a center of inversion), this result remains valid even when screening is taken into account.

Recently, a considerable number of papers have appeared in which light scattering in metals[1,2] and heavily doped semiconductors[3,4] is investigated experimentally. From these experiments it follows that, owing to the electron-phonon interaction, the electrons make an appreciable contribution to the frequency and damping of the optical phonons.

The theoretical work on the electron-phonon interaction in metals has been mainly concerned with acoustic phonons[5-10]. It has been shown that in metals there is an adiabatic parameter $\hbar\omega_D/E_F$ (ω_D is the Debye frequency and E_F is the Fermi energy), the existence of which makes it possible to calculate the electronic contribution to the acoustic-phonon spectrum in the whole range of phonon momenta q. The nonadiabatic correction to the spectrum is of order $(\hbar\omega_D/E_F)^2$.

In this paper we consider the renormalization of the optical-vibration frequencies that is due to the interaction with the electrons. Generally speaking, the interaction with the optical vibrations should not vanish in the long-wave limit ($q \to 0$)[11]. For semiconductors, such an interaction is well known, e.g., in n-Ge[11-13]. A direct calculation of the spectrum by expanding in powers of the pseudo-potential shows that in metals there is an effective interaction of the same type (see the Appendix). It is shown that, in the region of small phonon momenta $q \lesssim \hbar\omega_0/v_F$ (v_F is the Fermi velocity), a large (not containing the small parameter $\hbar\omega_0/E_F$) nonadiabatic correction to the bare optical-phonon frequency arises. Because of this, the frequencies of optical vibrations with $q < \hbar\omega_0/v_F$ and with $q > \hbar\omega_0/v_F$ should differ by an amount of the order of the coupling constant. It is shown that allowance for screening does not affect this result, for sufficiently symmetric crystals.

In the case of weak coupling, at $q = \hbar\omega_0/v_F$ we have the threshold for Landau damping for an optical phonon. With allowance for the screening, this threshold gives a singularity only in the derivative $\partial\omega_q/\partial q$ of the phonon frequency, i.e., in the group velocity of the phonons. In the case of strong coupling, the existence of the adiabatic parameter $\hbar\omega_0/E_F$ makes it possible to take a selection of diagrams and write a closed integral equation for the vertex part in the nonadiabatic region. The nonadiabatic renormalization turns out to be important for very small phonon momenta $q \ll q_{max}$. This region is manifested in the study of Raman scattering of light from laser sources.

1. INTERACTION OF ELECTRONS WITH LONG-WAVE OPTICAL VIBRATIONS

The role of the electron-phonon interaction is, generally speaking, different in metals and heavily doped semiconductors. In metals, the electrons play the determining role in shaping the forces that act between the ions of the crystal lattice. The acoustic branches of the vibrational spectrum of metals arise only because of the electron-ion interaction[7,8]. The electrons also make an important contribution to the optical-phonon spectrum[7,9]. As was shown in[6-10], the vibrational spectrum of metals can be found with good accuracy in the adiabatic approximation. In studying the nonadiabatic corrections due to the electron-phonon interaction, it is precisely this adiabatic spectrum that must be taken as the zeroth approximation.

In pure semiconductors, the phonon spectrum is shaped by the interatomic forces. On doping, a rearrangement of this spectrum occurs. If the vibration frequencies of the pure crystal are taken as the zeroth approximation, the electron-phonon interaction gives a large adiabatic renormalization of the spectrum and nonadiabatic corrections of the same type as in metals. Since in this paper we are studying the nonadiabatic renormalization of the optical-vibration frequencies in the region of very small phonon momenta ($q \ll q_{max} \approx p_F$), in the case of heavily doped semiconductors too it turns out to be convenient to take for the bare phonon frequency the frequency corresponding to the adiabatic approximation. One must keep in mind, however, that the adiabatic contribution of the electrons to the vibrational spectrum of semiconductors, unlike that in the case of metals, can also be observed experimentally.

To describe the electron-phonon interaction we shall make use of a Hamiltonian of the Fröhlich type:

$$H_{int} = \sum_{\mathbf{p},\mathbf{q},j} \langle \mathbf{p}|V_j(\mathbf{r})e^{i\mathbf{q}\mathbf{r}}|\mathbf{p}+\mathbf{q}\rangle a_{\mathbf{p}}^{+} a_{\mathbf{p}+\mathbf{q}} (b_{\mathbf{q}j} + b_{-\mathbf{q}j}^{+}), \qquad (1)$$

where $\langle \mathbf{p}|V_j(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}|\mathbf{p}+\mathbf{q}\rangle$ is a matrix element of the electron-phonon interaction, calculated using Bloch wavefunctions;

$$V_j(\mathbf{r}) = \sum_s V_s^{\alpha}(\mathbf{r})\xi_s^{\alpha}(\mathbf{q}, j),$$

where s labels the atom in the unit cell, $\xi_s^{\alpha}(\mathbf{q}, j)$ is the polarization vector of the lattice vibration of branch j with momentum $\mathbf{q}$; $b_{\mathbf{q}j}^{+}$ and $b_{\mathbf{q}j}$ are phonon creation and annihilation operators; $a_{\mathbf{p}}^{+}$ and $a_{\mathbf{p}}$ are electron creation and annihilation operators.

The possibility of using the Fröhlich Hamiltonian to calculate nonadiabatic corrections to the phonon frequencies found in the adiabatic approximation was discussed in[7,10]. It was shown that, to order $(\hbar\omega_0/E_F)^2$, the Hamiltonian (1) gives the correct renormalization of the spectrum, if from the renormalization found by

means of (1) we subtract the result obtained in the adiabatic limit (i.e., for $\omega_q/q \to 0$).

In the long-wave limits, the optical vibrations that we are considering reduce to a uniform displacement of the sublattices, which changes the electron wavefunctions. Therefore, generally speaking, the interaction with the optical vibrations should not vanish when $q \to 0$. In this case, the diagonal matrix elements $\langle \mathbf{p}|V_j(\mathbf{r})|\mathbf{p}\rangle \equiv V_j(\mathbf{p})$ depend in an essential way on the electron quasi-momentum $\mathbf{p}$. This dependence is determined by the symmetry of the long-wave optical vibration of branch j. Thus, e.g., in n-Ge the optical vibrations at the center of the Brillouin zone (q = 0) have the symmetry Γ_{25}^+. With allowance for the symmetry of the optical vibrations, the interaction with the electrons at the conduction-band minimum, positioned at the point $\mathbf{p}_{0i}$, should have the form

$$V_j(\mathbf{p}_{0i}) = \sqrt{\frac{\hbar}{2M\omega_0 N}} D \frac{1}{|p_{0i}|^2} [p_{0i}^x p_{0i}^y \xi_j^z + p_{0i}^x p_{0i}^z \xi_j^y + p_{0i}^y p_{0i}^z \xi_j^x], \qquad (2)$$

where D is the deformation-potential constant[1)].

In a crystal with a center of inversion, for lattice vibrations with q = 0, corresponding to even nonidentical representations of the group of the wave vector, the quantity $V_j(\mathbf{p})$ should satisfy the conditions

$$\sum_{\mathbf{p}} V_j(\mathbf{p})\delta(\varepsilon-\varepsilon_{\mathbf{p}}) = 0, \qquad (3)$$

$$\sum_{\mathbf{p}} V_j(\mathbf{p}) v^i \delta(\varepsilon-\varepsilon_{\mathbf{p}}) = 0. \qquad (4)$$

The condition (3) implies the absence of a change of electron density in a uniform displacement of the sublattices, and also means that the force exerted on each sublattice by the electrons in equilibrium is equal to zero. A similar condition for the interaction with a sound wave was discussed in [14]. The condition (4) corresponds to the absence of an electron current in the uniform displacement of the sublattices.

It can be seen that $V_j(\mathbf{p})$ from (2) automatically satisfies the conditions (3) and (4).

The optical-phonon spectrum is determined from the Dyson equation, which, for an isolated branch j, has the form [15]

$$D_j^{-1}(\mathbf{q}, \omega) = D_{0j}^{-1}(\mathbf{q}, \omega) - \Pi_j(\mathbf{q}, \omega), \qquad (5)$$

where $\Pi_j(\mathbf{q}, \omega)$ is the polarization operator, $D_j(\mathbf{q}, \omega)$ is the Green function of the lattice vibrations, and $D_{0j}(\mathbf{q}, \omega)$ is the zeroth-approximation Green function, equal to

$$D_{0j}(\mathbf{q}, \omega) = \omega_{\mathbf{q}j}^2/(\omega^2 - \omega_{\mathbf{q}j}^2 + i\delta). \qquad (6)$$

The frequencies of the phonon spectrum are determined by the equation $D_j^{-1}(\mathbf{q}, \omega) = 0$, whence, using (6), we have

$$\omega^2 = \omega_{\mathbf{q}j}^2[1 + \Pi_j(\mathbf{q}, \omega)]. \qquad (7)$$

According to the results of [7,10], when using for $\omega_{\mathbf{q}j}$ the frequency found in the adiabatic approximation we must replace $\Pi_j(\mathbf{q}, \omega)$ in (7) by $\tilde{\Pi}_j(\mathbf{q}, \omega)$, where

$$\operatorname{Re}\tilde{\Pi}_j(\mathbf{q}, \omega) = \operatorname{Re}\Pi_j(\mathbf{q}, \omega) - \operatorname{Re}\Pi_j(\mathbf{q}, 0), \qquad (8)$$

$$\operatorname{Im}\tilde{\Pi}_j(\mathbf{q}, \omega) = \operatorname{Im}\Pi_j(\mathbf{q}, \omega). \qquad (9)$$

2. CASE OF WEAK ELECTRON-PHONON INTERACTION

We shall discuss first the case of a weak electron-phonon interaction (1), treated by perturbation theory.

It is known that the dimensionless electron-phonon interaction constant for the acoustic vibrations in metals is of order unity [15]. A calculation, given in the Appendix, of the phonon spectrum by a direct expansion in powers of the pseudo-potential shows that for the optical phonons the interaction arises only in second order in the pseudo-potential. Therefore, the corresponding coupling constant turns out to be of order $(V_G/E_F)^2$, where V_G is the pseudo-potential of the metal ion. For the majority of non-transition metals, $V_G/E_F < 1$ and the interaction can be weak.

In heavily doped semiconductors, the coupling constant can also be assumed to be small, since this constant, analogously to the case of acoustic phonons, is proportional to the Fermi momentum $p_F \propto n^{1/3}$, and the electron concentration is usually two or three orders smaller than in metals.

In the lowest approximation of perturbation theory, $\Pi_j(\mathbf{q}, \omega)$ equals [15]

$$\Pi_j^0(\mathbf{q}, \omega) = -\frac{4}{\hbar\omega_{\mathbf{q}j}} \sum_{\mathbf{p}} \frac{V_j^2(\mathbf{p})(n_{\mathbf{p}+\mathbf{q}} - n_{\mathbf{p}})}{\hbar\omega - \varepsilon_{\mathbf{p}+\mathbf{q}} + \varepsilon_{\mathbf{p}} + i\operatorname{sgn}\omega}, \qquad (10)$$

where $n_{\mathbf{p}}$ are the occupation numbers and $\epsilon_{\mathbf{p}}$ are the electron energies.

The function $\Pi_j^0(\mathbf{q}, \omega)$ differs from the known expression for the polarization operator (cf., e.g., [15]) by the presence under the integral of the factor $V_j^2(\mathbf{p})$, which, however, does not change the character of the dependence of $\Pi_j^0(\mathbf{q}, \omega)$ on $\mathbf{q}$ and ω. This dependence is depicted qualitatively in Fig. 1.

In the region of small phonon momenta $q \ll q_{max}$ of interest to us, we have

$$\varepsilon_{\mathbf{p}+\mathbf{q}} - \varepsilon_{\mathbf{p}} \approx \mathbf{qv}, \quad n_{\mathbf{p}+\mathbf{q}} - n_{\mathbf{p}} \approx -\mathbf{qv}\delta(\varepsilon_{\mathbf{p}} - \varepsilon_F)$$

and it is convenient to rewrite (10) in the form

$$\Pi_j^0(\mathbf{q}, \omega) = \frac{4}{\hbar\omega_{0j}} \int \frac{ds}{|\nabla\varepsilon_p|} \frac{\mathbf{qv}_F}{\hbar\omega - \mathbf{qv}_F + i\operatorname{sgn}\omega} V_j^2(\mathbf{p}). \qquad (11)$$

where ds is an element of the Fermi surface.

Below, we shall consider the behavior of $\Pi_j^0(\mathbf{q}, \omega)$ in three regions.

1. $\mathbf{qv}_F > \hbar\omega_{0j}$. In this region,

$$\operatorname{Re}\Pi_j^0(\mathbf{q}, \omega) = -\frac{4}{\hbar\omega_{0j}} \int \frac{ds}{|\nabla\varepsilon_p|} V_j^2(\mathbf{p}) = -2\zeta_0,$$

$$\operatorname{Im}\Pi_j^0(\mathbf{q}, \omega) = -\frac{4\pi|\omega|}{\omega_{0j}} \int \frac{ds}{|\nabla\varepsilon_p|} V_j^2(\mathbf{p})\delta(\hbar\omega - \mathbf{qv}_F) \approx \pi\zeta_0 \frac{\hbar|\omega|}{qv_F} < 1.$$

According to (8) and (9), to terms of order $\hbar\omega_0/E_F$ the quantity $\tilde{\Pi} = 0$, and, thus, in this region the nonadiabatic renormalization is small (in agreement with the results of [6-10]).

2. $\mathbf{qv}_F < \hbar\omega_{0j}$. We have

$$\operatorname{Im}\Pi_j^0(\mathbf{q}, \omega) = 0, \quad \operatorname{Re}\Pi_j^0(\mathbf{q}, \omega) = 2\zeta_1(q\bar{v}_\parallel/\omega)^2;$$

$$\bar{v}_\parallel^2 = \int \frac{ds}{|\nabla\varepsilon_p|} v_\parallel^2, \quad \zeta_1 = \int \frac{ds}{|\nabla\varepsilon_p|} V_j^2(\mathbf{p}) v_\parallel^2 \frac{1}{2\bar{v}_\parallel^2}, \qquad (12)$$

$$\tilde{\Pi}_j^0 = 2[\zeta_0 + \zeta_1(q\bar{v}_\parallel/\omega)^2].$$

The quantity

$$\zeta_0 = \left(\frac{D_j a}{\hbar\omega_{0j}}\right)^2 \frac{m}{M} \frac{p_F a}{\hbar \cdot 2\pi^2} \qquad (13)$$

(D_j is the mean deformation-potential constant for the optical branch j) determines the difference between the

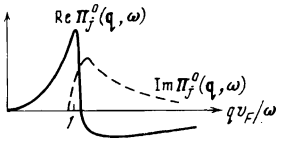

FIG. 1

adiabatic ($qv_F > \hbar\omega$) and the dynamical limit for the phonon frequency, and plays the role of the dimensionless parameter of the theory; $\zeta_1 \approx \zeta_0$.

Thus, in the region $qv_F < \hbar\omega$ there is a large nonadiabatic renormalization of the frequency, of order ζ_0, ζ_1:

$$\omega=\omega_0[1+\zeta_0+\zeta_1(q\bar{v}_\parallel/\hbar\omega)^2]. \tag{14}$$

3. $qv_F \lesssim \hbar\omega_0$. In this region $\mathrm{Re}\,\Pi_j^0(\mathbf{q}, \omega)$ has a maximum, associated with the presence of the pole in the integrand. The value of $\Pi_j^0(\mathbf{q}, \omega)$ near the maximum can be calculated by taking into account that the principal contribution to the integral over the Fermi surface in (11) is made in this case by the small region near the maximum value of $\mathbf{q}\cdot\mathbf{v}_F$[16]. For an arbitrary direction of $\mathbf{q}$, the quantity $\mathbf{q}\cdot\mathbf{v}_F$ has one maximum, and integration over the neighborhood of this maximum gives, with logarithmic accuracy,

$$\mathrm{Re}\,\Pi_j^0(\mathbf{q},\omega)=a\zeta_{p\,max}\ln\frac{c\omega}{\hbar\omega-qv_F}, \tag{15}$$

where a and c are constants of order unity;

$$\zeta_{pmax}=\frac{4p_{max}^2}{K|\nabla\varepsilon_{pmax}|\hbar\omega_{0j}}V_j^2(p_{max}), \tag{16}$$

where K is the Gaussian curvature at the maximum.

The case when $\mathbf{q}$ coincides with one of the symmetry directions of the crystal, and the quantity $\mathbf{q}\cdot\mathbf{v}_F$ has several equivalent maxima, requires a special analysis and will not be considered here.

3. EFFECT OF SCREENING

The optical vibrations change the electron distribution, and this, generally speaking, can lead to the appearance of an electric field. We shall consider for simplicity the case when $\omega_{0j}/v_F \gg \omega_p/c$, and confine ourselves to the region $q > \omega_p/c$. Under these conditions the transverse field that arises is small and can be disregarded[16]. Allowance for the longitudinal field reduces to replacing $\Pi_j^0(\mathbf{q}, \omega)$ by $[\Pi_j^0(\mathbf{q}, \omega)]_e$, where

$$[\Pi_j^0(\mathbf{q},\omega)]_e=\Pi_j^0(\mathbf{q},\omega)-\frac{4}{\hbar\omega_{qj}}\Big[\sum_p V_j(\mathbf{p})\frac{n_{p+q}-n_p}{\hbar\omega-\mathbf{qv}+i\,\mathrm{sgn}\,\omega}\Big]^2\frac{4\pi e^2}{q^2\varepsilon(\mathbf{q},\omega)} \tag{17}$$

and the dielectric constant $\epsilon(\mathbf{q}, \omega)$ equals (cf.[15])

$$\varepsilon(\mathbf{q},\omega)=1-\frac{4\pi e^2}{q^2}\sum_p\frac{n_{p+q}-n_p}{\hbar\omega-\mathbf{qv}+i\,\mathrm{sgn}\,\omega}. \tag{18}$$

As can be seen from (17), in the adiabatic region $\omega \ll qv_F$ the term responsible for the screening vanishes by virtue of the condition (3) and, thus, does not change the magnitude of the phonon frequency. In the region $\omega \gg qv_F$, when the condition (4) is taken into account $[\Pi_j^0(\mathbf{q}, \omega)]_e$ takes the form

$$[\Pi_j^0(\mathbf{q},\omega)]_e=\frac{q^2}{\omega^2}\Big[\int\frac{ds}{|\nabla\varepsilon_p|}V_j^2(\mathbf{p})v_\parallel^2 - \Big(\int\frac{ds}{|\nabla\varepsilon_p|}v_\parallel^2\Big)^{-1}\Big(\int\frac{ds}{|\nabla\varepsilon_p|}V_j(p)v_\parallel^2\Big)^2\Big]. \tag{19}$$

The expression in the square brackets in (19) is nonzero and, thus, the region of strong dispersion at low q also remains when screening is taken into account.

Near the threshold for Landau damping, $qv_F \lesssim \hbar\omega_0$, the principal contribution to the integrals appearing in (17) for $[\Pi_j^0(\mathbf{q}, \omega)]_e$ is made by the region of integration near the maximum of $\mathbf{q}\cdot\mathbf{v}$. Calculation of the integrals with logarithmic accuracy shows that the logarithmic singularity in the spectrum is screened:

$$\mathrm{Re}[\Pi_j^0(\mathbf{q},\omega)]_e\approx b\zeta_{pmax}(\hbar\omega-qv_F)\ln\frac{c\omega}{\hbar\omega-qv_F}, \tag{20}$$

and only a singularity in the derivative $(\partial\omega/\partial q)_{\hbar\omega=(qv)_{max}} \to \infty$ remains.

4. CASE OF STRONG ELECTRON-PHONON INTERACTION

Estimating, following Migdal[5], the correction to the vertex part of the electron-phonon interaction, we convince ourselves that for optical phonons in the region $\hbar\omega_0 \gtrsim qv_F$ this correction is of order ζ_0 and has no adiabatic small factor $\hbar\omega_0/E_F$. In the principal region of variation of the momentum, $q > q_0 = \hbar\omega_0/v_F$, the correction to the vertex part is, as before, small ($\sim\hbar\omega_0/E_F$). In this same region, the results of the perturbation-theory calculation of the electronic contribution to the optical-phonon frequency are valid, since this contribution is determined by electrons far from the Fermi surface. The nonadiabatic renormalization of the phonon spectrum in this region is, as before, small ($\sim(\hbar\omega_0/E_F)^2$). The spectrum of the electrons near the Fermi surface is strongly renormalized by the interaction with the phonons. The region of small phonon momenta in this case is in no way distinct and has no effect on the electron spectrum. Thus, to quantities of order $\hbar\omega_0/E_F$, we have[5,10]

$$\varepsilon=\varepsilon_p+\Sigma(\varepsilon,\mathbf{p}), \tag{21}$$

$$\mathrm{Re}\,\Sigma(\varepsilon,\mathbf{p})=\frac{\zeta_0}{4p_0\langle V_j^2(\mathbf{p},\mathbf{k})\rangle}\int_0^{k_1}\omega_{\mathbf{k}j}V_j^2(\mathbf{p},\mathbf{k})\ln\Big|\frac{\varepsilon+\hbar\omega_k}{\varepsilon-\hbar\omega_k}\Big|\,k\,dk,$$
$$\mathrm{Im}\,\Sigma(\varepsilon,\mathbf{p})=\frac{\pi\zeta_0}{4p_0^2\langle V_j^2(\mathbf{p},\mathbf{k})\rangle}\int_0^{k_1}V_j^2(\mathbf{p},\mathbf{k})\,\omega_{\mathbf{k}j}k\,dk, \tag{22}$$

where $\omega_{\mathbf{k}j}$ is the phonon frequency calculated in the adiabatic approximation. According to (21), (22) the optical phonons give a large ($\sim\zeta_0$) contribution to the renormalization of the velocity near the Fermi surface. The damping due to optical phonons in the region $\epsilon < \hbar\omega_{j,\min}$ is small ($\sim\zeta_0(\epsilon^2/E_F\omega_0)$), but becomes large ($\sim\zeta_0$) for $\epsilon > \hbar\omega_{j,\min}$.

The calculation of the optical-phonon spectrum in the region $q < \hbar\omega_0/v_F$ requires the determination of the exact vertex part $\Gamma_j(p, q)$ of the electron-phonon interaction. The quantity $\Gamma_j(p, q)$ satisfies the equation (see also Fig. 2)

$$\Gamma_j(p,q)=V_j(p,q)+i\int\frac{d^4p'}{(2\pi)^4}K(p,p',q)G(p')G(p'+q)\Gamma_j(p',q), \tag{23}$$

where K(p, p′, q) is the irreducible vertex part of the interaction between the electrons, which does not contain $D_j(q)$ and the singular elements G(p)G(p + q) having a pole at small q. The perturbation-theory series for the quantity K(p, p′, q) is represented in Fig. 3. The wavy line corresponds to the phonon Green function found in the adiabatic approximation. For this reason, diagrams of the type depicted in Fig. 4 are already taken into account in the initial adiabatic spectrum and do not appear in the series for K(p, p′, q)[10].

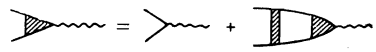

FIG. 2

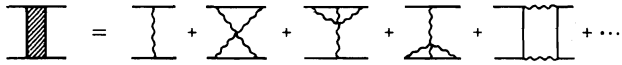

FIG. 3

FIG. 4

Examination of the terms in the series for K(p, p′, q) shows that for $\omega \approx \omega_0$, $qv_F \approx \hbar\omega \ll E_F$, diagram a in Fig. 3 gives the maximum contribution (of order ζ_0) to K(p, p′, q). The contribution of the other diagrams is of order $\sim \hbar\omega/E_F$, which appears in the integration of the extra function D(k) with a nonresonance denominator. Thus, in the region $qv_F \lesssim \hbar\omega$, the quantity $\Gamma_j(p, q)$ can be found from the solution of the linear integral equation

$$\Gamma_j(p,q) = V_j(p) + i\int \frac{d^4p}{(2\pi)^4} K^0(p,p')G(p')G(p'+q)\Gamma_j(p,q), \quad (24)$$

where

$$K^0(p,p') = \frac{V_j^2(\mathbf{p},\mathbf{p}')\,\omega^2_{\mathbf{p}-\mathbf{p}',j}}{(\varepsilon-\varepsilon')^2-\omega^2_{\mathbf{p}-\mathbf{p}',j}}, \quad (25)$$

and the function G(p) is expressed in the well-known way in terms of the self-energy part $\Sigma(\epsilon, \mathbf{p})$ already found (see (21), (22)).

An integral equation of the type (24) was obtained earlier by Engelsberg and Schrieffer[6], who considered a model in which the electron-phonon interaction does not depend on p and the phonon branch has no dispersion. For a model with a scalar interaction (independent of p), it can be shown[6,15] that $\Pi_j(\mathbf{q}, \omega)|_{q=0} = 0$; however, this result does not remain valid for the p-dependent interaction that we are considering. To determine the limiting dynamical ($q \to 0$, $q/\omega_q \to 0$) optical-phonon frequency, we therefore need the solution of the integral equation for $\Gamma_j^{\omega}(\mathbf{p}, \omega)$:

$$\Gamma_j^{\omega}(\mathbf{p},\omega) = V_j(\mathbf{p}) + i\int \frac{d^4p'}{(2\pi)^4} K^0(\mathbf{p},\mathbf{p}')[G^2(\mathbf{p}')]^{\omega}\Gamma_j^{\omega}(\mathbf{p}',\omega). \quad (26)$$

The limiting value of the optical-phonon frequency is determined by the formulas

$$\omega^2 = \omega_{0j}^2[1+\Pi_j(\omega)], \quad (27)$$

$$\Pi_j(\omega) = -2i\int V_j(\mathbf{p})[G^2(\mathbf{p})]^{\omega}\Gamma_j^{\omega}(\mathbf{p},\omega)\frac{d^4p}{(2\pi)^4}. \quad (28)$$

The dispersion of the branch in the region of small momenta is determined by equations of the Fermi-liquid theory type[15]:

$$\Pi_j(\mathbf{q},\omega) = \Pi_j(\omega) + i\int \Gamma_j^{\omega}(\mathbf{p},\omega)\,(G(\mathbf{p}+\mathbf{q})G(\mathbf{p}) - [G^2(p)]^{\omega})\Gamma_j(\mathbf{p},\mathbf{q})\frac{d^4p}{(2\pi)^4}, \quad (29)$$

$$\Gamma_j(\mathbf{p},\mathbf{q}) = \Gamma_j^{\omega}(\mathbf{p},\omega) + i\int \Gamma_j^{\omega}(\mathbf{p},\omega)\,(G(\mathbf{p}+\mathbf{q})G(\mathbf{p}) - [G^2]^{\omega})\Gamma_j(\mathbf{p},\mathbf{q})\frac{d^4p}{(2\pi)^4}. \quad (30)$$

To solve these equations requires a special analysis. The difficulties in solving Eqs. (24), (26) and (29) are associated primarily with the fact that, in the frequency region of interest, the renormalization of the electron spectrum (the dependence of the velocity of the excitations on the energy) and also the energy dependence of $K^0(p, p', q)$ turn out to be important.

Hence we can conclude that the renormalizations of the optical-phonon frequencies in the regions $\hbar\omega_{0j} < qv_F$ and $\hbar\omega_{0j} > qv_F$ differ by an amount of the order of $\omega_0\zeta_0$:

$$\omega_{qj}|_{qv_F < \hbar\omega_0} - \omega_{qj}|_{qv_F > \hbar\omega_0} \approx \zeta_0\omega_{0j}.$$

It can also be shown that, in the nonadiabatic region, the optical-phonon damping can turn out to be small. The principal damping mechanism in this region is decay into a phonon with large momentum and an electron-hole pair. If the total dispersion of the optical branch in the whole region of momenta $q \lesssim q_{max}$ is sufficiently great, $\omega_{j,max} - \omega_{0j} > \omega_{0j}$, where $\omega_{j,max}$ is the limiting short-wave optical-phonon frequency, this decay process will be limited by the low phonon density in the final state. The dispersion of an optical branch in the nonadiabatic region has the order of the quantity $\zeta_0(qv_F/\hbar\omega_0)^2$.

5. DISCUSSION OF THE RESULTS

The region of the nonadiabatic renormalization of the optical-vibration spectrum corresponds to small momenta $q \lesssim \hbar\omega_0/v_F \ll q_{max}$. It is precisely this region of momenta that is manifested in light-scattering experiments. Investigations of this kind have become possible recently in connection with the use of laser light sources.

Light scattering in metals and heavily doped semiconductors occurs in the thin layer defined by the depth δ of penetration of the light into the crystal. In a metal this is the skin-depth, and in a semiconductor it is length determined by the magnitude of the absorption coefficient at the given frequency. Violation of the momentum conservation law for the wave-vector component perpendicular to the surface of the sample leads in this case to the result that all phonons with $q \lesssim \hbar/\delta$ make a contribution to the light-scattering cross-section[17].

In the case of metals, usually $\delta \approx 10^{-6}$ cm in the optical region, and since $v_F \approx 10^8$ cm·sec^{-1} and $\omega_0 \approx 10^{13}$ sec^{-1}, we have $\hbar/\delta > q_0 = \hbar\omega_0/v_F$. Therefore, both the adiabatic and the nonadiabatic regions of the optical-vibration spectrum make a contribution to the scattering. For $\hbar/\delta \gg q_0$ the contribution of the adiabatic region should dominate. The large temperature-independent Raman-scattering linewidth $\gamma \approx 0.1\omega_0$, which is experimentally observable in a whole series of metals, can be explained by the strong Landau damping for the optical branch in the region $q \gtrsim \hbar\omega_0/v_F$. In metals, it would be interesting to investigate experimentally the case $\hbar/\delta \approx q_0$, which, in the visible region, can probably be realized for metals with a sufficiently large skin-depth and large optical-vibration frequency. The optical-branch frequency observable in the scattering should differ in this case from that found by neutron-diffraction methods. As shown in[18], in this case an asymmetric scattering line should be observed, with a tail on the short-wave side, due to the strong dispersion of the branch in the nonadiabatic region.

Studies of scattering by lattice vibrations in heavily doped semiconductors are of great interest[3,4]. The electronic properties of these materials are in many respects suggestive of metals[19]. An important point is that the electron concentration in them is a variable parameter and we can investigate the concentration dependences. In the high-frequency region in n-Ge with $n \sim 7 \times 10^{20}$ cm^{-3} and $v_F \approx 10^7$ cm·sec^{-1}, $\delta \approx 10^{-4}$ cm, the optical-phonon frequency $\omega_0 \approx 10^{14}$ sec^{-1} and, thus, $\hbar/\delta < q_0$. In these conditions, only the nonadiabatic reg-

ion contributes to the scattering. The interaction with the optical phonons that has been studied in this paper, which does not vanish as $q \to 0$, is realized in n-Ge[11,20]. Light-scattering experiments in heavily doped n-Ge[4] have not exhibited an appreciable concentration shift or asymmetry of the Raman-scattering line. It may be thought, therefore, that the case $1/\delta \ll q_0$ is realized in[4], i.e., the extreme long-wave part of the nonadiabatic region makes a contribution to the scattering. In addition, in n-Ge the coupling constant $\zeta_0 < 1$, and this also reduces the effect. For Ge it would also be useful to study the region $\hbar/\delta \approx q_0$, in which asymmetry of the line and a concentration shift should appear. Realization of the condition $\hbar/\delta \approx q_0$ should be facilitated by increasing the concentration, and also by using laser lines with frequencies in the region of large values of the absorption coefficient (small δ).

APPENDIX

Following[7-9], we shall calculate the contribution of the electrons to the dynamical matrix $D_{ss'}^{\alpha\beta}(\mathbf{q}, \omega)$ of the crystal, which determines the vibrational spectrum. The quantity $D_{ss'}^{\alpha\beta}(\mathbf{q}, \omega)$ can be calculated by means of perturbation theory in the pseudo-potential. In contrast to[7], to determine $D_{ss'}^{\alpha\beta}(\mathbf{q}, \omega)$ we shall use the Dyson equation directly, choosing the Green function of the vibrations of a lattice of free particles as the initial function. In this case, the polarization operator of the Dyson equation coincides with the dynamical matrix $D_{ss'}^{\alpha\beta}(\mathbf{q}, \omega)$ of the lattice.

In the lowest (second) order in the pseudo-potential, the contribution of the electrons to the polarization operator is determined by the diagram in Fig. 5. Allowance for the electron-electron Coulomb interaction reduces to the fact that, in one of the vertices, the pseudo-potential must be divided by the corresponding $\epsilon(\mathbf{q}, \omega)$. The contribution of the diagram in Fig. 5 has the form

$$D_{ss'}^{\alpha\beta}(\mathbf{q}, \omega) = \frac{1}{Mv_0} \sum_{\mathbf{q},\mathbf{G}} \frac{|V_{\mathbf{q}+\mathbf{G}}|^2 (\mathbf{q}+\mathbf{G})^\alpha (\mathbf{q}+\mathbf{G})^\beta}{\varepsilon(\mathbf{q}+\mathbf{G}, \omega)} \exp(i\mathbf{q}\rho_{ss'}) \Pi(\mathbf{q}+\mathbf{G}, \omega), \tag{A.1}$$

where $\mathbf{G}$ is a reciprocal-lattice vector and $V_{\mathbf{q}}$ is a Fourier component of the pseudo-potential. For estimates of the quantity $\Pi(\mathbf{q}, \omega)$ it is sufficient to take a thin loop, in which the lines correspond to free-electron Green functions:

$$\Pi(\mathbf{q}+\mathbf{G}, \omega) = \sum \frac{n_{\mathbf{p}+\mathbf{q}+\mathbf{G}} - n_{\mathbf{p}}}{\hbar\omega + E_{\mathbf{p}} - E_{\mathbf{p}+\mathbf{q}+\mathbf{G}}}. \tag{A.2}$$

In the sum over $\mathbf{G}$ in (A.1) there is no term with $\mathbf{G} = 0$, since, from the neutrality condition, $V_{\mathbf{G}|\mathbf{G}=0} = 0$.

For small $\mathbf{q}$ the difference appearing in the denominator in (A.2) is $E_{\mathbf{p}+\mathbf{q}+\mathbf{G}} - E_{\mathbf{p}} \approx E_F$, and, since $\hbar\omega \ll E_F$, we have

$$\Pi(\mathbf{G}, \omega) = \Pi(\mathbf{G}, 0) + O[(\hbar\omega/E_F)^2]. \tag{A.3}$$

Thus, in the lowest (second) order in the pseudo-potential, the limiting frequency coincides with its adiabatic limiting value.

In the next order (the third) in the pseudo-potential, the polarization operator is determined by the diagram in Fig. 6. The corresponding contribution to $D_{ss'}^{\alpha\beta}(\mathbf{q}, \omega)$ equals

$$D_{ss'}^{\alpha\beta}(\mathbf{q}, \omega)|_{q\to 0} = \sum_{\mathbf{G}\mathbf{G}_1\mathbf{G}_2} \frac{V(\mathbf{G}) V(\mathbf{G}_1) V(\mathbf{G}_2)}{\varepsilon(G)\varepsilon(G_1)\varepsilon(G_2)} G^\alpha G_1^\beta S(\mathbf{G}_2) \times \exp(i\mathbf{G}\rho_s - \mathbf{G}_1\rho_s) \Delta(\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}) \Lambda^3(\mathbf{G}, \mathbf{G}_1, \mathbf{G}_2; \omega), \tag{A.4}$$

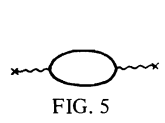

FIG. 5

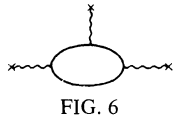

FIG. 6

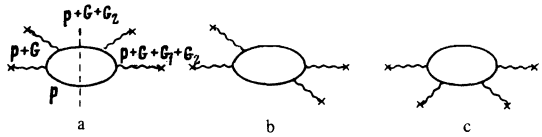

FIG. 7

where $\Lambda^3(\mathbf{G}, \mathbf{G}_1, \mathbf{G}_2; \omega)$ is the irreducible three-point function. In this expression, $\mathbf{G}, \mathbf{G}_1, \mathbf{G}_2 \neq 0$ and $\mathbf{G}_1 + \mathbf{G}_2 = -\mathbf{G}$. From Fig. 6 it can be seen that terms with the following denominators make a contribution to Λ^3:

$$(E_{\mathbf{p}+\mathbf{G}+\mathbf{q}} - E_{\mathbf{p}})(E_{\mathbf{p}+\mathbf{G}-\mathbf{G}_1+\mathbf{q}} - E_{\mathbf{p}} + \hbar\omega), \quad (E_{\mathbf{p}+\mathbf{G}+\mathbf{q}} - E_{\mathbf{p}} + \hbar\omega)(E_{\mathbf{p}+\mathbf{G}-\mathbf{G}_1+\mathbf{q}} - E_{\mathbf{p}+\mathbf{q}+\mathbf{G}}),$$
$$(E_{\mathbf{p}+\mathbf{q}+\mathbf{G}-\mathbf{G}_1} - E_{\mathbf{p}+\mathbf{q}+\mathbf{G}})(E_{\mathbf{p}+\mathbf{q}+\mathbf{G}-\mathbf{G}_1} - E_{\mathbf{p}} - \hbar\omega).$$

Since only terms with $\mathbf{G}, \mathbf{G}_1, \mathbf{G}_2 \neq 0$ make a contribution to the limiting optical frequency, the electron-energy differences in the denominators are of the order of the Fermi energy, and the phonon frequency ω can be neglected. The nonadiabatic correction will contain the small parameter $(\hbar\omega/E_F)^2$.

A different situation arises in the next order (the fourth) in the pseudo-potential. The corresponding diagrams are shown in Fig. 7. Here, in $D_{ss'}^{\alpha\beta}(\mathbf{q}, \omega)$, as before, $\mathbf{G}, \mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3 \neq 0$ and $\mathbf{G}_1 + \mathbf{G}_2 + \mathbf{G}_3 = -\mathbf{G}$. Amongst the other contributions to $D_{ss'}^{\alpha\beta}(\mathbf{q}, \omega)$, the term containing the denominator corresponding to the section cut by the dashed line in Fig. 7a requires special treatment. For $\mathbf{G} = -\mathbf{G}_2$, this energy denominator behaves as follows:

$$E_{\mathbf{p}} - E_{\mathbf{p}+\mathbf{q}+\mathbf{G}+\mathbf{G}_2} + \hbar\omega|_{\mathbf{G}=-\mathbf{G}_2} = \hbar\omega - \mathbf{q}\mathbf{v}. \tag{A.5}$$

The same denominators also arise in the terms corresponding to the diagrams in Fig. 7b and 7c. In (A.5) the quantity ω can be neglected in comparison with $\mathbf{q}\cdot\mathbf{v}$ only when $\hbar\omega \ll \mathbf{q}\cdot\mathbf{v}$. In the region $\hbar\omega \approx \mathbf{q}\cdot\mathbf{v}_F$ the dependence on ω is important, and this indicates the existence of a nonadiabatic region for the optical phonons.

For a crystal with sufficiently high symmetry, containing two atoms per unit cell, the dynamical matrix is easily diagonalized in the indices of the Cartesian coordinates. The corresponding frequency correction, which has a large nonadiabatic part, is equal to

$$\Delta\omega_\alpha^2(\mathbf{q}\to 0) = \sum_{\mathbf{G},\mathbf{G}_1,\mu} G^\alpha G_1^\alpha \frac{V^2(\mathbf{G}) V^2(\mathbf{G}_1)}{\varepsilon^2(\mathbf{G})\varepsilon^2(\mathbf{G}_1)} \sin\mathbf{G}\rho \sin\mathbf{G}_1\rho \times \frac{[\hbar\omega - 2(E_{\mathbf{p}+\mathbf{G}} - E_{\mathbf{p}})][\hbar\omega - 2(E_{\mathbf{p}+\mathbf{G}_1} - E_{\mathbf{p}})]}{(\hbar\omega - E_{\mathbf{p}+\mathbf{G}} + E_{\mathbf{p}})(\hbar\omega - E_{\mathbf{p}+\mathbf{G}_1} + E_{\mathbf{p}})} \frac{n_{\mathbf{p}+\mathbf{q}} - n_{\mathbf{p}}}{\hbar\omega - \mathbf{q}\mathbf{v}}. \tag{A.6}$$

The expression (A.6) is conveniently rewritten in the form

$$\Delta\omega_\alpha^2(\mathbf{q}\to 0) = \sum_{\mathbf{p}} (V_{\mathbf{p}}^\alpha)^2 \frac{n_{\mathbf{p}+\mathbf{q}} - n_{\mathbf{p}}}{\hbar\omega - \mathbf{q}\mathbf{v}}, \tag{A.7}$$

where $V_{\mathbf{p}}^\alpha$ is the effective vertex of the interaction, and depends on $\mathbf{p}$:

$$V_{\mathbf{p}}^\alpha = \sum_{\mathbf{G}} G^\alpha \frac{V_{\mathbf{G}}^2 \sin\rho\mathbf{G}[\hbar\omega - 2(E_{\mathbf{p}+\mathbf{G}} - E_{\mathbf{p}})]}{\varepsilon^2(G)[\hbar\omega - (E_{\mathbf{p}+\mathbf{G}} - E_{\mathbf{p}})][E_{\mathbf{p}+\mathbf{G}} - E_{\mathbf{p}}]}. \tag{A.8}$$

In $V_{\mathbf{p}}^\alpha$ we must neglect $\hbar\omega$ in comparison with E_F; then,

$$V_{\mathbf{p}}^\alpha = \sum_{\mathbf{G}} G^\alpha \frac{V_\alpha^2 \cdot 2\sin\mathbf{G}\rho}{\varepsilon^2(G)(E_{\mathbf{p}+\mathbf{G}} - E_{\mathbf{p}})}. \tag{A.9}$$

The resulting correction to the frequency coincides with expression (10) of this article.

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[1)] In a number of papers (see, e.g., [12,13]), the interaction with the optical phonons in n-Ge has been used in the form

$$V_j(\mathbf{p}) = V\frac{1}{|p_{0i}|}\sum_{\alpha} p_{0i}^{\alpha}\xi_j^{\alpha},$$

which contradicts the symmetry requirements. The difference in the form of the interaction is not manifested in calculations of the relaxation times but turns out to be important when screening is considered.

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