Long-wavelength optical phonons: damping, surface oscillations, and Raman scattering

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A self-consistent system of equations is derived for conduction electrons interacting with long-wavelength optical phonons in polar and nonpolar metals. The damping and renormalization of the optical phonon spectrum due to this interaction are found. The long-range electric field in a polar crystal is taken into account, and the effects of the Coulomb interaction of the carriers are studied. The dispersion relation for surface optical phonons, in contrast to acoustic Rayleigh waves, displays two branches. The computed response of the phonon system to an arbitrary external field in a semi-infinite anisotropic crystal (metal and dielectric) is used to determine the Raman scattering cross section of light accompanied by the excitation and absorption of phonons. © *1995 American Institute of Physics.*

1. INTRODUCTION

Interest in optical phonons and the electron–phonon interaction in different structures has recently arisen in connection with experiments on Raman scattering, electron spectroscopy, and so on. However, existing phenomenological models encounter difficulties, especially when attempts are made to take surface effects into account.[1] Moreover, as a rule, the simplest isotropic Frölich model is used for the electron–phonon interaction.

Long-wavelength acoustic phonons in metals are ordinarily described by means of the so-called dynamical theory of elasticity (see, for example, Ref. 2). The theory employs self-consistent equations (taking into account the electron–lattice interaction) of the theory of elasticity for phonons and the kinetic equation for electrons. In the present work we propose similar equations for optical phonons.

To derive these equations, we take the long-wavelength limit of the microscopic Lagrangian, constructed on the basis of a dynamical matrix, and we distinguish among the optical degrees of freedom. By varying the action we obtain the desired equation for the optical phonons together with the boundary condition for the action. The boundary condition leads to the existence of surface optical phonons (whose existence was discussed previously only in the case of an isotropic nonpolar dielectric[3]).

In Sec. 2 an equation is derived for optical phonons by the method indicated above. The effects of electron–phonon, electron–impurity, and electron–electron interactions—renormalization and damping of optical phonons—are discussed in Sec. 3. In Sec. 4 a semi-infinite crystal is studied: the spectrum of surface optical phonons is found and the response to an external perturbation is calculated. The results obtained are used in Sec. 5 to calculate the Raman scattering cross section for phonons; Brillouin–Mandel'shtam scattering of light in metals accompanied by the excitation of acoustic phonons was studied in Ref. 4.

2. EQUATION OF MOTION FOR OPTICAL PHONONS INTERACTING WITH ELECTRONS

We use the deformation potential to describe the interaction of the electrons with optical phonons.[5] In other words, we assume that a relative displacement w_i^s of the sublattices produces a local change in the electron spectrum:

$$\varepsilon(\mathbf{p},\mathbf{r},t)=\varepsilon_0(\mathbf{p})+\xi_i^s(\mathbf{p})w_i^s(\mathbf{r},t), \tag{1}$$

where $\varepsilon_0(\mathbf{p})$ is the spectrum of the undeformed crystal and $\xi^s(\mathbf{p})$ are the deformation-potential vectors, whose number s is one less than the number of sublattices. In what follows, we confine our attention to the case of two sublattices.

In many cases, the quasiclassical approximation can be used to describe the electronic excitations. We shall therefore use the distribution function $f_p(\mathbf{r},t)$ which satisfies the kinetic equation.

The complete Lagrangian of the metal, including the interaction (1), has the form

$$\begin{aligned}L(\mathbf{r},t)=&\frac{\rho}{2}\dot{w}_i^2(\mathbf{r},t)-\frac{\rho}{2}\chi_{il}w_i(\mathbf{r},t)w_l(\mathbf{r},t)\\&-\frac{1}{2}\mu_{iklm}\frac{\partial w_i(\mathbf{r},t)}{\partial x_k}\frac{\partial w_l(\mathbf{r},t)}{\partial x_m}\\&-2w_i(\mathbf{r},t)\int\frac{d^3p}{(2\pi)^3}\xi_i(\mathbf{p})f_p(\mathbf{r},t)\\&+qw_i(\mathbf{r},t)E_i(\mathbf{r},t)+L_{e-pl}(\mathbf{r},t).\end{aligned} \tag{2}$$

Here, L_{e-pl} is the Lagrangian of the electronic excitations in an electromagnetic field. The first term is the kinetic energy of the relative motion of the sublattices; the second and third terms represent the long-wavelength expansion of the dynamical matrix; ρ is the reduced-mass density; q is the density of the effective ionic charge; χ_{ik} and μ_{iklm} are tensors of the elastic constants, whose order of magnitude is

$$\chi_{ik}=\chi_{ki}\simeq\omega_D, \quad \mu_{iklm}=\mu_{lmik}=\mu_{kilm}\simeq\rho s^2,$$

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where ω_D is the Debye frequency and s is the speed of sound.

The third term in the Lagrangian (2) is the long-wavelength limit of the small dispersion correction, and in contrast to the acoustic case, it need not have a definite sign.[6] At the same time, this term is important, since it leads to the boundary condition for and the dispersion of optical phonons. The one before the last term, representing the interaction of the dipole moment of the sublattices with the electric field, is absent in a nonpolar metal.

Varying the action corresponding to the Lagrangian (2) gives the equation of motion of the sublattices

$$\rho\ddot{w}_i(\mathbf{r},t)-\mu_{iklm}\frac{\partial^2 w_l(\mathbf{r},t)}{\partial x_k\partial x_m}+\rho\chi_{il}w_l(\mathbf{r},t)$$

$$=-2\int\frac{d^3p}{(2\pi)^3}\,\xi_i(\mathbf{p})f_p(\mathbf{r},t)+qE_i(\mathbf{r},t) \tag{3}$$

with the boundary condition

$$\mu_{iklm}\frac{\partial w_l}{\partial x_m}l_k=0, \tag{4}$$

where l_k is the normal to the surface. The condition (4) replaces the condition that the normal stress vanishes, which the displacement of the surface satisfies in the theory of elasticity.

3. BULK OPTICAL PHONONS

Boltzmann's equation for the electron distribution function

$$\frac{\partial f_p(\mathbf{r},t)}{\partial t}+\mathbf{v}\frac{\partial f_p(\mathbf{r},t)}{\partial\mathbf{r}}+\dot{\mathbf{p}}\frac{\partial f_p(\mathbf{r},t)}{\partial\mathbf{p}}=\hat{S}tf_p(\mathbf{r},t) \tag{5}$$

can be linearized by making the substitution

$$f_p(\mathbf{r},t)=f_0(\epsilon(\mathbf{p},\mathbf{r},t)-\mu_0)+\frac{df_0}{d\epsilon}\,\delta f_p(\mathbf{r},t). \tag{6}$$

The argument of the equilibrium distribution function $f_0(\epsilon-\mu_0)$ is chosen so that the collision integral $\hat{S}tf_p(\mathbf{r},t)$ vanishes to zeroth order in $\delta f_p(\mathbf{r},t)$. We use the relaxation time approximation for the collision integral (the possibility of neglecting the arrival term in the collision integral is discussed in detail in Ref. 7).

We consider first an infinite crystal, and we expand all quantities in Fourier integrals. Equation (5) then assumes the form

$$-i(\omega-\mathbf{vk}+i\tau_p^{-1})\delta f_p(\mathbf{k},\omega)$$

$$=i\omega\xi_i(\mathbf{p})w_i(\mathbf{k},\omega)-ev_iE_i(\mathbf{k},\omega). \tag{7}$$

We use Poisson's equation

$$\epsilon_{ik}^0\frac{\partial^2}{\partial x_i\partial x_k}\phi(\mathbf{r},t)=-8\pi e\int\frac{d^3p}{(2\pi)^3}\,f_p(\mathbf{r},t)$$

$$-4\pi q\frac{\partial}{\partial x_i}w_i(\mathbf{r},t), \tag{8}$$

where ϵ_{ik}^0 is the permittivity of the filled bands, to describe the electric field $\mathbf{E}(\mathbf{r},t)=-\text{grad}\,\phi(\mathbf{r},t)$, which contains both the Coulomb interaction of the carriers and the field generated by the dipole moment of the sublattices. Substituting Eqs. (6) and (7), we obtain

$$\phi(\mathbf{k},\omega)=\frac{4\pi e}{D(\mathbf{k},\omega)}\left\langle\frac{\xi_i(\mathbf{p})\mathbf{vk}}{\omega-\mathbf{vk}+i\tau_p^{-1}}\right\rangle w_i(\mathbf{k},\omega)$$

$$-\frac{4\pi iqk_i}{D(\mathbf{k},\omega)}\,w_i(\mathbf{k},\omega), \tag{9}$$

where

$$D(\mathbf{k},\omega)=\epsilon_{ik}^0k_ik_k-4\pi e^2\left\langle\frac{\mathbf{vk}}{\omega-\mathbf{vk}+i\tau_p^{-1}}\right\rangle, \tag{10}$$

and the brackets denote integration over the Fermi surface:

$$\langle\cdots\rangle=2\int(\ldots)\frac{dS_F}{(2\pi)^3v}.$$

The region of applicability of Poisson's equation for three-dimensional problems in metals is quite wide and is determined by the condition $ck\gg\omega_p$, where ω_p is the plasma frequency. It is applicable in dielectrics near the intersection of the photon and phonon branches of the spectrum $\omega_D\simeq ck/\epsilon^{1/2}$. Generally speaking, Maxwell's equation must be used to study surface plasmon-polaritons—this was done in Ref. 8 for a nonpolar metal, and the polar case must be studied separately.

An equation determining the spectrum and the damping of bulk optical excitations is obtained by substituting Eq. (9) into Eq. (7) and then into Eq. (3):

$$(\rho\chi_{il}+\mu_{iklm}k_kk_m-\rho\omega^2\delta_{il})w_l(\mathbf{k},\omega)$$

$$=-\left\langle\frac{\xi_i(\mathbf{p})\xi_l(\mathbf{p})(\mathbf{vk}-i\tau_p^{-1})}{\omega-\mathbf{vk}+i\tau_p^{-1}}\right\rangle w_l(\mathbf{k},\omega)$$

$$-\frac{4\pi e^2}{D(\mathbf{k},\omega)}\left\langle\frac{\xi_i(\mathbf{p})(\mathbf{vk}-i\tau_p^{-1})}{\omega-\mathbf{vk}+i\tau_p^{-1}}\right\rangle$$

$$\times\left\langle\frac{\xi_l(\mathbf{p})\mathbf{vk}}{\omega-\mathbf{vk}+i\tau_p^{-1}}\right\rangle w_l(\mathbf{k},\omega)-\frac{4\pi q^2k_ik_l}{D(\mathbf{k},\omega)}\,w_l(\mathbf{k},\omega). \tag{11}$$

We consider two cases.

a) Nonpolar metal: $q=0$

In the absence of the electron–phonon interaction ($\xi_i(\mathbf{p})=0$), the dispersion relation has the simple form

$$|\rho\chi_{il}+\mu_{iklm}k_kk_m-\rho\omega^2\delta_{il}|=0 \tag{12}$$

and for the isotropic case

$$\chi_{il}=\omega_D^2\delta_{il},$$

$$\mu_{iklm}=\rho a_t(\delta_{il}\delta_{km}+\delta_{im}\delta_{kl})+\rho(a_l-2a_t)\delta_{ik}\delta_{lm} \tag{13}$$

it gives dispersion of the longitudinal and transverse optical phonons near threshold:

$$\omega^2(\mathbf{k})=\omega_D^2+a_{l,t}k^2,$$

where $a_l=\mu_{xxxx}/\rho$ and $a_t=\mu_{xzxz}/\rho$.

The second term on the right-hand side of Eq. (11) represents the Coulomb interaction of the electrons. It deter-

mines the renormalization of the deformation potential in the first term on the right-hand side of Eq. (11). For $vk \gg |\omega + i\tau^{-1}|$, renormalization obviously means making the replacement

$$\xi_l(\mathbf{p}) \to \xi_l(\mathbf{p}) - \frac{\langle \xi_l(\mathbf{p}) \rangle}{\langle 1 \rangle}.$$

The first term on the right-hand side of Eq. (11) describes the damping and renormalization of the elastic constants as a result of the interaction of optical oscillations with electrons. This happens differently in the short- and long-wavelength limits.

Over a wide range $vk \gg |\omega + i\tau^{-1}|$, the real and imaginary parts of the first term yield a renormalization of the Debye frequency

$$\chi_{il} \to \chi_{il} - \frac{\langle \xi_i(\mathbf{p}) \xi_l(\mathbf{p}) \rangle}{\rho} \tag{14}$$

and the damping $\Gamma(\mathbf{k})$ of the optical phonons

$$\Gamma_{def}(\mathbf{k}) \simeq \frac{\pi}{2\rho k} \left\langle \frac{\xi^2(\mathbf{p}) \delta(\nu)}{v} \right\rangle, \tag{15}$$

where $\nu = \mathbf{vk}/vk$. We write the index "*def*" to emphasize the deformation origin of this damping. Taking damping into account, the dispersion of the phonons can be written in the form $\omega = \omega(\mathbf{k}) - i\Gamma(\mathbf{k})$. Setting $\xi \simeq \epsilon_F p_F$, we obtain

$$\Gamma_{def}(\mathbf{k}) \simeq \frac{\omega_D^2}{vk}. \tag{16}$$

In the long-wavelength limit $vk \ll |\omega + \tau^{-1}|$, the displacement of the threshold frequency and the damping are

$$\delta\chi_{il} = -\frac{\langle \xi_i(\mathbf{p}) \xi_l(\mathbf{p}) \rangle}{\rho(\omega^2\tau^2 + 1)}, \tag{17}$$

$$\Gamma_{def}(\mathbf{k}) \simeq \frac{\tau}{2\rho} \frac{\langle \xi^2(\mathbf{p}) \rangle}{\omega^2\tau^2 + 1} \simeq \frac{\omega_D^2 \tau}{\omega^2\tau^2 + 1}. \tag{18}$$

The collisionless limit $vk\tau \gg 1$ [see Eq. (15)] was studied in Ref. 9 by means of the diagrammatic technique.

In Ref. 10 Brovman and Kagan discussed the renormalization of the phonon spectra as a result of the interaction with electrons. According to their results, the renormalization (14) and (17) must be corrected by subtracting its value at $\omega = 0$, which is responsible for the adiabatic nature of the electron–phonon system.

We note that the damping of optical phonons is appreciably different from that of acoustic phonons. It depends strongly on the parameter $\omega\tau$, which is absent from the expression for the damping of sound.[11]

The frequency range $\omega \sim vk$ merits special attention. As the frequency ω approaches $v_{\max}k$, where $v_{\max}$ is the maximum value of the projection of the Fermi velocity on the direction $\mathbf{k}$, a singularity appears on the right-hand side of Eq. (11) for small values of τ^{-1}. The Coulomb interaction of the electrons (second term) weakens this singularity substantially. To logarithmic accuracy

$$\left\langle \frac{\xi_i(\mathbf{p}) \mathbf{vk}}{\omega - \mathbf{vk}} \right\rangle = -\langle \xi_i(\mathbf{p}) \rangle + \xi_{i0} \langle 1 \rangle \ln(\alpha/x),$$

where $x = 1 - v_{\max}k/\omega > 0$; the subscript "0" designates the value of $\xi_i(\mathbf{p})$ at the point where $\mathbf{vk} = v_{\max}k$; for $x < 0$ the term $\ln(x)$ must be replaced by $\ln|x| + i\pi$. For $(\omega_D\tau)^{-1} \ll |x| \ll 1$ we obtain for the frequency shift and damping

$$\delta\chi_{il} \simeq -\frac{\langle (\xi_i(\mathbf{p}) - \xi_{i0})(\xi_l(\mathbf{p}) - \xi_{l0}) \rangle}{\rho},$$

$$\Gamma_{def}(\mathbf{k}) \simeq \frac{\pi}{2\rho\omega_D} \langle (\xi_i(\mathbf{p}) - \xi_{i0})(\xi_l(\mathbf{p}) - \xi_{l0}) \rangle \frac{\theta(x)}{\ln^2|\alpha/x|}.$$

Here $\theta(x)$ is the Heaviside unit step function. Therefore, as a result of the Coulomb interaction, the optical phonons remain weakly damped excitations even when they fall into the range of one-pair electronic excitations.

b) Polar metal: $q \neq 0$

In a polar crystal, besides the effects described in section *a* and deformation effects, additional renormalization and damping of optical phonons represented by the last term in Eq. (11) can occur. In an isotropic dielectric, this term gives the well-known shift of the longitudinal phonon frequency $\omega_0^2 \to \omega_l^2 = \omega_0^2 + 4\pi q^2/\rho\epsilon$.

The situation is different in a metal: the effects associated with polarity are negligible compared to the deformation effects.

Calculation shows that for short-wavelengths $vk \gg |\omega + i\tau^{-1}|$ and under conditions such that $k \ll p_F$, there arises a renormalization of the dispersion parameter

$$\delta\mu_{iklm} = \frac{q^2}{e^2\langle 1 \rangle} \delta_{ik}\delta_{lm} \simeq \rho s^2 \tag{19}$$

and a contribution

$$\Gamma_{pol}(\mathbf{k}) \simeq \frac{\pi q^2 k}{2\rho e^2 \langle 1 \rangle^2} \left\langle \frac{\delta(\nu)}{v} \right\rangle \tag{20}$$

to the damping appears. Comparing the expression (20) to Eq. (15), we obtain

$$\Gamma_{pol}/\Gamma_{def} \simeq (k/p_F)^2 \ll 1.$$

In the long-wavelength limit $vk \ll |\omega + i\tau^{-1}|$ in a metal, as in a dielectric, it is not the dispersion parameter that is renormalized, but the threshold in the spectrum of optical phonons:

$$\delta\chi_{pol} \simeq \frac{q^2}{e^2\langle v^2 \rangle} (\omega^2 - \tau^{-2}) \simeq \frac{s^2}{v^2} (\omega_D^2 - \tau^{-2}). \tag{21}$$

The sign of the expression (21) depends on the value of $\omega\tau$, and $|\delta\chi_{pol}/\delta\chi_{def}| \simeq (s/v)^2 \max(1, (\omega\tau)^{-1}) \ll 1$. In this same case the damping is

$$\Gamma_{pol}(\mathbf{k}) \simeq \frac{q^2}{\tau\rho e^2 \langle v^2 \rangle}. \tag{22}$$

Comparing Eqs. (22) and (18), we find $\Gamma_{pol}/\Gamma_{def} \simeq (\epsilon_F\tau)^{-1}$. Therefore, for electronic excitations in a metal, the polar contribution to the damping is always small com-

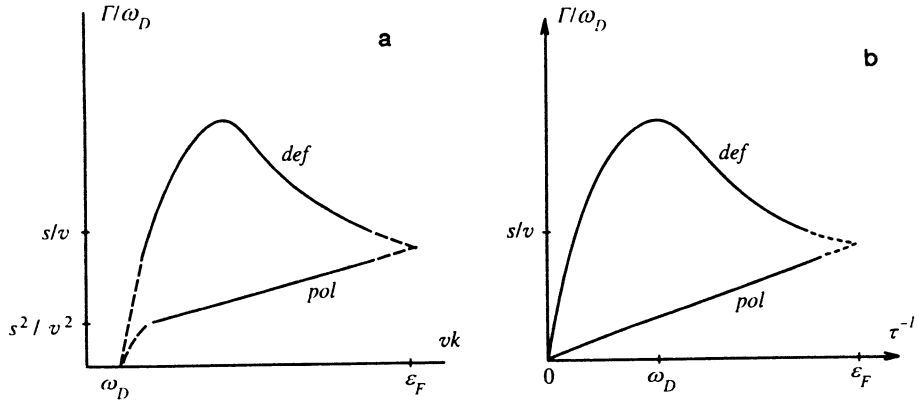

FIG. 1. Deformation and polar contributions to the attenuation of optical phonons: a) short wavelengths $vk \gg |\omega + i\tau^{-1}|$; b) long wavelengths $vk \ll |\omega + i\tau^{-1}|$.

pared to the deformation contribution. The characteristic dependence of the damping of the optical photons on ω, vk, and τ^{-1} is displayed in Fig. 1.

4. SURFACE OPTICAL PHONONS

We now calculate the response of a semi-infinite ($z>0$) crystal to an arbitrary perturbation $U(\mathbf{r},\omega)$ described by the Hamiltonian

$$H = -\int d^3r\, \eta_i w_i(\mathbf{r},\omega) U(\mathbf{r},\omega) \tag{23}$$

with some vertex η_i. The term $\eta_i U(\mathbf{r},\omega)$ must be added to the right-hand side of Eq. (3) in this case.

To solve the equation of motion so obtained, we continue the component of the displacement $w_s(s,z,\omega)$ parallel to the surface and the field $U(s,z,\omega)$ into the region $z<0$ as even functions, and the perpendicular component $w_z(s,z,\omega)$ as an odd function:

$$w_s(s,z<0,\omega) = w_s(s,-z,\omega),$$

$$w_z(s,z<0,\omega) = -w_z(s,-z,\omega),$$

$$U(s,z<0,\omega) = U(s,-z,\omega).$$

All quantities can then be expanded in spatial Fourier integrals:

$$\mathbf{w}(k_s,k_z,\omega) = \int_{-\infty}^{\infty} ds \int_0^{\infty} dz\, \mathbf{w}(s,z,\omega) e^{-ik_s s} \times (e^{-ik_z s} \pm e^{ik_z z}).$$

When the Fourier components in Eq. (3) are calculated, singularities arise on the surface $z=0$ that are associated with derivatives with respect to z. These singularities result in the appearance of additional terms, which represent surface effects.

We now assume that the surface of the crystal is a symmetry plane and that the wave of displacements propagates along a principal axis. This means that the tensor components with an odd number of z indices are equal to zero. The equation for the displacement component perpendicular to the sz plane is not coupled to the other two. This component does not participate in the surface oscillations and will not be considered below.

In the s equation, the singularity at the surface is given by the expression

$$-\mu_{szsz} \frac{\partial^2 w_s}{\partial z^2} - (\mu_{szsz} + \mu_{sszz}) \frac{\partial^2 w_z}{\partial s\, \partial z},$$

which leads to the appearance of a surface term that does not depend on k_z:

$$-2\mu_{szsz} \frac{\partial w_s}{\partial z}(z=0^+) + 2ik_s(\mu_{szsz} + \mu_{sszz}) w_z(z=0^+).$$

In the z equation, the special term

$$-\mu_{zzzz} \frac{\partial^2 w_z}{\partial z^2},$$

yields a term linear in k_z:

$$2ik_z \mu_{zzzz} w_z(z=0^+).$$

Therefore, in Fourier components Eq. (3) has the form

$$(\rho\chi_{\alpha l}(\mathbf{n}) + \mu_{\alpha klm} k_k k_m - \rho\omega^2 \delta_{\alpha l}) w_l(\mathbf{k},\omega) = \eta_\alpha U(\mathbf{k},\omega) + k_\alpha C_\alpha(k_s,\omega), \tag{24}$$

where there is no summation over Greek indices, and the coefficients $C_\alpha(k_s,\omega)$, which are linear combinations of $\partial\omega_s(0^+)/\partial z$ and $\omega_z(0^+)$, must be found from the boundary condition (4). We included the damping in ω: $\omega \to \omega + i\Gamma$, and all renormalizations are included in the elastic moduli. As a result, the tensor χ_{ik} depends on the direction $\mathbf{n}$ of the vector $\mathbf{k}$.

The zeros of the determinant of the matrix on the left-hand side of Eq. (24) give the spectrum of bulk optical waves—in the isotropic case these are longitudinal and transverse phonons:

$$\omega^2 = \omega_l^2 + a_l k^2, \quad \omega^2 = \omega_t^2 + a_t k^2,$$

where

$$\omega_l^2 = \chi_{il} n_i n_l, \quad \omega_t^2 = \tfrac{1}{2}\chi_{il}(\delta_{il} - n_i n_l). \tag{25}$$

The solution of Eq. (24) has the form

$$w_l(\mathbf{k},\omega) = D_{lk}^{\infty}(\mathbf{k},\omega)\, \eta_k U(\mathbf{k},\omega) + \sum_\alpha D_{l\alpha}^{\infty}(\mathbf{k},\omega) k_\alpha C_\alpha(k_s,\omega), \tag{26}$$

where we have introduced the Green's function matrix $D^{\infty}_{ik}(\mathbf{k},\omega)$ of a phonon in an infinite crystal. This matrix satisfies the equation

$$(\rho\chi_{il}+\mu_{iklm}k_k k_m-\rho\omega^2\delta_{il})D^{\infty}_{ln}(\mathbf{k},\omega)=\delta_{in}. \tag{27}$$

We determine the constants $C_\alpha(k_s,\omega)$ from the boundary condition (4):

$$C_\alpha(k_s,\omega)=D^{(s)}_{\alpha i}(k_s,\omega)\mu_{izlm}\times\int\frac{dk_z}{2\pi}D^{\infty}_{lk}(\mathbf{k},\omega)\eta_k U(\mathbf{k},\omega)k_m, \tag{28}$$

where $D^{(s)}_{\alpha i}(k_s,\omega)$ is the "surface" Green's function matrix, which satisfies the equation

$$\sum_\alpha D^{s}_{\alpha k}(k_s,\omega)\mu_{izlm}\int\frac{dk_z}{2\pi}D^{\infty}_{l\alpha}(\mathbf{k},\omega)k_m k_\alpha e^{ik_z z}=-\delta_{ik}. \tag{29}$$

Equations (26)–(29) give the solution of the problem posed. The first term in Eq. (26) is the response of an infinite crystal to the external field $U(\mathbf{k},\omega)$. The poles of $D^{\infty}_{ik}(\mathbf{k},\omega)$ determine the spectrum of the bulk phonons.

For the isotropic case we find

$$D^{\infty}_{ik}(\mathbf{k},\omega)=\frac{1}{\rho a_l a_t(k_z^2+\kappa_l^2)(k_z^2+\kappa_t^2)}\times\begin{pmatrix} a_l k_z^2+a_t\kappa_t^2 & -(a_l-a_t)k_s k_z \\ -(a_l-a_t)k_s k_z & a_t k_z^2+a_l\kappa_l^2\end{pmatrix}, \tag{30}$$

where

$$\kappa_{l,t}^2=k_s^2-(\omega^2-\omega_{l,t}^2)/a_{l,t}; \tag{31}$$

the $\omega_{l,t}$ are given by the expressions (25), and the $a_{l,t}$ are given by Eq. (13). We took into account the fact that in an isotropic crystal the excitation thresholds of longitudinal and transverse phonons are different because of the renormalizations: $\omega_l\neq\omega_t$.

The second term in Eq. (26) is the surface contribution. The poles of $D^{s}_{ik}(k_s,\omega)$ determine the surface optical waves—the analog of Rayleigh acoustic waves.

We now give an expression, which will be required below, for the tensor

$$D^{(s)}_{\alpha z}\mu_{zz\beta\beta}=-\frac{2\omega^2\kappa_l\rho}{a_t^2[(k_s^2+\kappa_t^2)^2-4k_s^2\kappa_t\kappa_l]}\times\begin{pmatrix}(a_l-2a_t)^2 & (a_l-2a_t)a_l\\ (a_l-2a_t)a_l & a_l^2\end{pmatrix}. \tag{32}$$

According to Eq. (32), the spectrum of surface optical phonons is determined by the equation

$$(k_s^2+\kappa_t^2)^2-4k_s^2\kappa_t\kappa_l=0. \tag{33}$$

This equation has the same form as the dispersion relation for Rayleigh waves,[6] except that here κ_l and κ_t are given by (31).

In the special case $\omega_l=\omega_t$, Eq. (33) yields two branches of surface optical phonons [see Fig. 2(a)]: one (dispersionless)

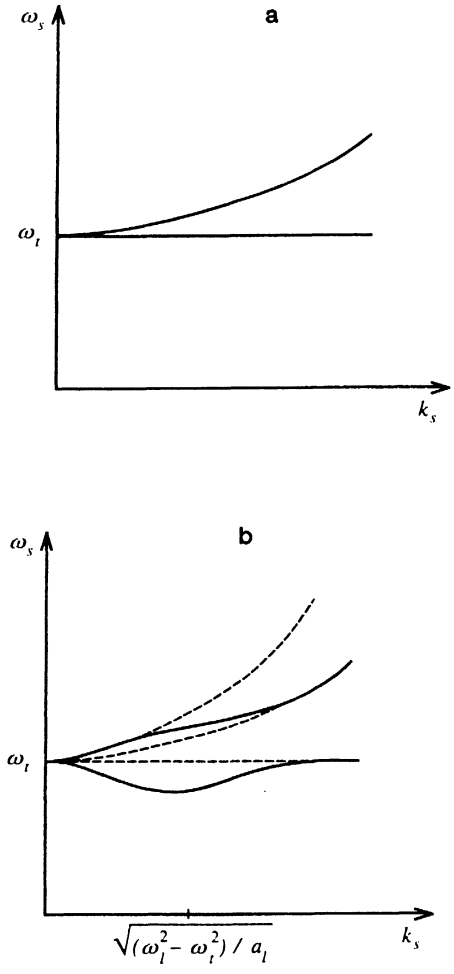

FIG. 2. Spectrum of surface optical phonons ($a_l>0$, $a_t>0$). a) $\omega_l=\omega_t$; b) $\omega_l\neq\omega_t$. The dashed lines represent the curves $\omega^2=\omega_t^2$, $\omega^2=\omega_t^2+a_s k_s^2$, and $\omega^2=\omega_t^2+a_t k_s^2$.

$$\omega_s^2(k_s)=\omega_t^2, \tag{34}$$

and another (with quadratic dispersion)

$$\omega_s^2(k_s)=\omega_t^2+a_s k_s^2, \tag{35}$$

where a_s is related to a_l and a_t by the same algebraic equation as for Rayleigh waves,[6] and s_R^2 is related to s_l^2 and s_t^2:

$$\left(\frac{a_s}{a_t}\right)^3-8\left(\frac{a_s}{a_t}\right)^2+8\left(3-2\frac{a_t}{a_l}\right)\frac{a_s}{a_t}-16\left(1-\frac{a_t}{a_l}\right)=0. \tag{36}$$

For any ratio of a_l and a_t, Eq. (36) has a unique root corresponding to real values of $\kappa_{l,t}$, such that $|a_s|\ll|a_l|$, $|a_t|$. The amplitude of the surface oscillations (34) and (35) decreases with depth exponentially at distances of the order of the wavelength $\simeq k_s^{-1}$.

For $\omega_l\neq\omega_t$, two surface waves also exist. Their spectrum is displayed in Fig. 2b. In the long-wavelength limit $k_s^2\ll(\omega_l^2-\omega_t^2)/a_l$, the dispersion curves are given by

$$\omega_s^2(k_s)=\omega_t^2-4^{2/3}a_t\left(\frac{\omega_l^2-\omega_t^2}{a_l}\right)^{2/3}k_s^{4/3},$$

$$\omega_s^2(k_s)=\omega_t^2+a_t k_s^2-\frac{a_t a_l}{16(\omega_l^2-\omega_t^2)}\,k_s^4.$$

We note that these surface oscillations exist if $(\omega_l-\omega_t)/a_l>0$. Normal to the surface, the longitudinal components of the surface waves decay exponentially at distances $\kappa_l^{-1}=(a_l/(\omega_l^2-\omega_t^2))^{1/2}$, and the transverse components decay over much larger distances $\kappa_t^{-1}=\kappa_l^{-1/3}k_s^{-2/3}$ for the first component and $4\kappa_l/k_s^2$ for the second component.

If $\omega_l-\omega_t$ is small compared to the characteristic Debye frequencies, then a region where $a_l k_s^2 \gg \omega_l^2-\omega_t^2$ can exist. Here, the dispersion curves reach the values (34) and (35) [Fig. 2(b)].

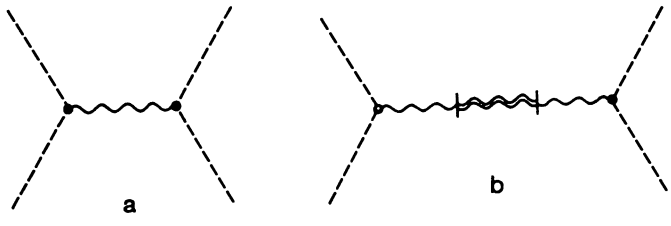

FIG. 3. Diagrammatic representation of the Raman scattering cross section of (a) bulk optical phonons and (b) surface optical phonons. The dashed lines represent the incident ($A^{(i)}$) and scattered ($A^{(s)}$) photons; the dot represents the phonon–photon vertex η_i; the wavy line represents the bulk phonon Green's function D_{ik}^{∞}; the double wavy line represents the surface Green's function D_{ik}^{s}.

5. RAMAN SCATTERING

Raman scattering of light is due both to conduction electrons and to electrons in filled shells. In a previous paper we studied the first contribution, consisting of the electron–hole continuum and the phonon peaks resulting from electron–phonon interaction.[7] We use Placzek's phenomenological approach to describe the contribution of the electrons in filled shells as scattering by permittivity fluctuations (see Ref. 12). The polarizability of the atomic shells and the permittivity ϵ_{ik}^0 depend on the deformation

$$\epsilon_{ik}^0=\epsilon_{ik}^0(\mathbf{w}). \tag{37}$$

The effective Hamiltonian that describes the scattering of light is obtained from the Hamiltonian of the electric field in a crystal in which the dependence of the permittivity on the lattice displacements is taken into account. Expanding the expression (37) in powers of w_i, we obtain

$$H=\frac{1}{4\pi c^2}\int d^3r\,\eta_i w_i(\mathbf{r},t)A^{(i)}(\mathbf{r},t)A^{(s)}(\mathbf{r},t), \tag{38}$$

where

$$\eta_i=\left.\frac{\partial\epsilon_{kl}^0(\mathbf{w})}{\partial w_i}\right|_{w=0} e_k^{(i)}e_l^{(s)},$$

$e_k^{(i)}$, $A^{(i)}(\mathbf{r},t)$ and $e_l^{(s)}$, $A^{(s)}(\mathbf{r},t)$ are the polarization and vector potential of the incident and scattered light, respectively. It should be noted that these quantities are different in a crystal from their values in free space, and they are determined by the solution of the electrodynamic boundary value problem of the distribution of the incident and scattered light.[8]

The scattering cross section in the frequency interval $d\omega^{(s)}$ and solid angle interval $do^{(s)}$ of the scattered light has the form

$$\frac{d\sigma}{d\omega^{(s)}do^{(s)}}=\frac{k_z^{(s)}\omega^{(s)}}{2\omega^{(i)2}\pi^3c^3}\,\eta_i^*\eta_k\int dzdz'K_{ik}(k_s,z,z',\omega)\times U^*(k_s,z,\omega)U(k_s,z',\omega), \tag{39}$$

where $K_{ik}(k_s,z,z',\omega)$ is the Fourier transform of the correlation function

$$\langle\langle w_i(\mathbf{r},t)w_k(\mathbf{r}',t')\rangle\rangle. \tag{40}$$

Here, the brackets represent statistical averaging; the effective external field is $U(\mathbf{r},t)=A^{(i)}(\mathbf{r},t)A^{(s)}(\mathbf{r},t)\propto\exp(-i\omega t+ik_s s)$, and the transmitted frequency and wave vector parallel to the surface $\omega=\omega^{(i)}-\omega^{(s)}$ and $k_s=k_s^{(i)}-k_s^{(s)}$ have been introduced.

To calculate the correlation function (40), we use the fluctuation–dissipation theorem:

$$K_{ik}(k_s,z,z',\omega)=\frac{1}{1-\exp(-\omega/T)}\,\mathrm{Im}\;\alpha_{ik}(k_s,z,z',\omega).$$

The generalized susceptibility α_{ik}, defined by the relation

$$w_i(k_s,k_z,\omega)=\int\frac{dk_z'}{2\pi}\,\alpha_{ik}(k_s,k_z,k_z',\omega)\,\eta_k U(k_s,k_z',\omega),$$

can be found by means of Eqs. (26)–(29):

$$\alpha_{ik}(k_s,k_z,k_z',\omega)=2\pi D_{ik}^{\infty}(k_s,k_z,\omega)\,\delta(k_z-k_z')+\sum_{\alpha\beta}D_{i\alpha}^{\infty}(k_s,k_z,\omega)k_\alpha D_{\alpha z}^{s}(k_s,\omega)\times\mu_{zz\beta\beta}k_\beta' D_{\beta k}^{\infty}(k_s,k_z',\omega). \tag{41}$$

The first term in Eq. (41) represents scattering by bulk phonons [Fig. 3(a)], and the second term represents scattering by surface phonons [Fig. 3(b)].

We note that the contribution of the conduction electrons to Raman scattering[7] can be taken into account by adding to η_i the term

$$-\frac{4\pi e^2}{m}\left\langle\frac{\gamma(\mathbf{p})\xi_i(\mathbf{p})(\mathbf{vk}-i\tau_p^{-1})}{\omega-\mathbf{vk}-i\tau_p^{-1}}\right\rangle, \tag{42}$$

which is represented by the diagram in Fig. 4.

The contribution of optical bulk phonons to the cross section for an isotropic crystal has the form

$$\frac{d\sigma}{d\omega^{(s)}do^{(s)}}\propto\mathrm{Im}\int\frac{dk_z}{2\pi}\,|U(\mathbf{k},\omega)|^2\eta_i^*\eta_k D_{ik}^{\infty}(\mathbf{k},\omega), \tag{43}$$

where the proportionality factor [see Eq. (39)] is

$$\frac{k_z^{(s)}\omega^{(s)}}{2\omega^{(i)2}\pi^3c^3}\,\frac{1}{1-\exp(-\omega/T)}.$$

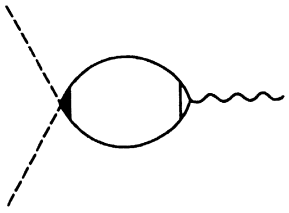

FIG. 4. Effective phonon–photon vertex for electron Raman scattering. The solid line represents the electron Green's function; the dark triangle represents the electron–photon vertex $\gamma(\mathbf{p})$; the open triangle represents the electron–phonon vertex $\xi_i(\mathbf{p})$.

We shall not write it out explicitly below. The factor $U(\mathbf{k},\omega)$, describing the exponential character of the distribution of the incident and scattered light, has the form[8]

$$U(\mathbf{k},\omega)=\frac{2i(\zeta_1+i\zeta_2)}{(\zeta_1+i\zeta_2)^2-k_z^2}, \tag{44}$$

where $\zeta_1+i\zeta_2$ is the sum of the normal components of the wave vectors of the incident and scattered radiation in the crystal. The quantity ζ_2 is determined by the attenuation of the light in the medium (by the imaginary part of the refractive index). For normal incidence and scattering, Eq. (43) gives

$$\frac{d\sigma}{d\omega^{(s)}do^{(s)}}\propto \mathrm{Im}\int \frac{dk_z}{2\pi\rho}\frac{|\eta_s|^2|U(\mathbf{k},\omega)|^2}{\omega_t^2+a_tk_z^2-(\omega+i\Gamma)^2}. \tag{45}$$

The denominator in Eq. (45) has a minimum of width Δk_z at $k_z=k_{\max}$:

$$k_{\max}^2=(\omega^2-\omega_t^2)/a_t,\quad \Delta k_z=|\omega\Gamma/(a_t(\omega^2-\omega_t^2))^{1/2}|, \tag{46}$$

where the damping Γ is given by (15) and (18) when the scattering is due to a metallic sample. We now consider two limiting cases in the typical situation $\zeta_1\gg\zeta_2$.

a) Strong attenuation, $\Delta k_z\gg\zeta_2$. Then, only $|U|^2$, taking the denominator at $k_z=\zeta_1$, need be integrated:

$$\frac{d\sigma}{d\omega^{(s)}do^{(s)}}\propto\frac{\Gamma|\eta_s|^2}{2\rho\zeta_2\omega_t[(\omega-(\omega_t^2+a_t\zeta_1^2)^{1/2})^2+\Gamma^2]}. \tag{47}$$

The expression (47) has the form of a peak, describing the excitation of a transverse phonon with frequency $\omega=(\omega_t^2+a_t\zeta_1^2)^{1/2}$ and momentum $k_z=\zeta_1$.

b) Weak attenuation, $\Delta k_z\ll\zeta_2$. Integrating only the denominator and taking $|U|^2$ at $k_z=k_{\max}$, we obtain

$$\frac{d\sigma}{d\omega^{(s)}do^{(s)}}\propto\frac{|\eta_s|^2}{2a_l\rho(2\omega_t)^{1/2}[(k_{\max}-\zeta_1)^2+\zeta_2^2]}\times\mathrm{Re}\left(\frac{a_l}{\omega-\omega_t+i\Gamma}\right)^{1/2}, \tag{48}$$

where

$$\mathrm{Re}\left(\frac{a}{\omega-\omega_t+i\Gamma}\right)^{1/2}=|a|^{1/2}\left(\frac{(\omega-\omega_t)\operatorname{sgn}a+[(\omega-\omega_t)^2+\Gamma^2]^{1/2}}{(\omega-\omega_t)^2+\Gamma^2}\right)^{1/2}.$$

The expression (48) has the form of a split peak. One maximum is located at the threshold $\omega=\omega_t$, and the other is located at $\omega=\omega_{op}(k_s=0,k_z=\zeta_1)$, and is given by energy and momentum conservation. These maxima are resolved in frequency: the interval between them is $\simeq a_t\zeta_1^2/2\omega_t$, while their width is $\simeq a_t\zeta_1\zeta_2/2\omega_t$.

For oblique propagation of light ($k_s\neq0$), together with excitation of a transverse phonon (47) and (48), there exists a peak that corresponds to the excitation of a longitudinal optical phonon. It can be analyzed similarly. It is described by formulas similar to Eqs. (47) and (48). We give the relative magnitude of the corresponding cross sections:

$$\frac{\sigma_l}{\sigma_t}\simeq\min\left(\frac{k_s^2}{\zeta_1^2},1\right).$$

In the general case, the heights of all peaks are of the same order of magnitude.

The second term in Eq. (41) represents the contribution of surface phonons to the Raman scattering cross section. Substituting into Eq. (39), we obtain

$$\frac{d\sigma}{d\omega^{(s)}do^{(s)}}\propto\mathrm{Im}\sum_{\alpha\beta}D_{\alpha z}^{(s)}(k_s,\omega)\times\mu_{zz\beta\beta}I_\alpha^*(k_s,\omega)I_\beta(k_s,\omega), \tag{49}$$

where

$$I_\alpha(k_s,\omega)=\sum_\gamma\int\frac{dk_z}{2\pi}\eta_\gamma U(\mathbf{k},\omega)D_{\gamma\alpha}^\infty(\mathbf{k},\omega)k_\gamma, \tag{50}$$

and the Green's function matrices $D_{ik}^\infty(\mathbf{k},\omega)$ and $D_{ik}^s(\mathbf{k}_s,\omega)$ are given in the isotropic case by Eqs. (30) and (32).

In the range $\omega^2<\omega_{l,t}^2+a_{l,t}k_s^2$, both κ_l and κ_t are real. This means that both the transverse and longitudinal oscillations decay away from the surface. According to Eq. (32), an imaginary part in Eq. (49) appears near the poles corresponding to the excitation of surface optical phonons. The corresponding peak is Lorentzian:

$$\frac{d\sigma}{d\omega^{(s)}do^{(s)}}\propto\frac{\Gamma|\eta_s|^2}{\rho a^{1/2}\max(k_s^2,|\zeta|^2)[(\omega-\omega_s(k_s))^2+\Gamma^2]}. \tag{51}$$

In the range $\omega_t^2+a_tk_s^2<\omega^2<\omega_l^2+a_lk_s^2$, κ_t becomes imaginary—transverse phonons can propagate throughout the crystal. Once again, longitudinal phonons decay away from the surface. The contribution of these quasisurface excitations has the form of a narrow continuum arising in a square-root fashion near the threshold $\kappa_t=0$:

$$\frac{d\sigma}{d\omega^{(s)}do^{(s)}}\propto\frac{|\eta_s|^2}{\rho a^{3/2}k_s^2\max(k_s^2,|\zeta|^2)}(\omega^2-\omega_t^2-a_tk_s^2)^{1/2}. \tag{52}$$

In the case $\omega_l^2+a_l k_s^2<\omega^2$, both κ_l and κ_t are imaginary: both longitudinal and transverse phonons propagate throughout. In this case the cross section has a peak associated with the excitation of longitudinal phonons sliding along the surface. This peak is asymmetric:

$$\frac{d\sigma}{d\omega^{(s)}do^{(s)}}\propto\frac{|\eta_s|^2}{\rho k_s^{1/2}a^{3/4}|\zeta|^2}\times\left(\frac{\delta\omega\ \mathrm{sgn}\ a_l+(\delta\omega^2+\Gamma^2)^{1/2}}{\delta\omega^2+\Gamma^2}\right)^{1/2},\qquad(53)$$

where $\delta\omega=\omega-(\omega_l^2+a_l k_s^2)^{1/2}$.

6. CONCLUSIONS

In the present paper we examined in detail optical phonons in metals and dielectrics. The attenuation of these phonons is substantially different from that of acoustic phonons. It was found that surface optical phonons with characteristic frequencies ~1 THz exist. In contrast to the well-known surface Rayleigh waves, there exist two branches of such oscillations, which are described by a nonlinear dispersion law. These excitations, like bulk optical phonons, can be observed in experiments on Raman scattering of light. The width of the peaks associated with the excitation of surface oscillations is always less than the width of volume peaks, since it is determined exclusively by their characteristic attenuation. The decay constant of the incident electromagnetic field also contributes to the width of the bulk peaks.

It is well known that besides these excitations, there also exist surface plasmon–polaritons. These excitations must be analyzed separately.

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