Electron-Phonon Interaction in Dielectric Films. Application to Electron Energy Loss and Gain Spectra

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The classical analysis, due to Kliewer and Fuchs, of the optical polarization modes of an ionic crystal film in the long-wavelength limit is used to develop a quantum-mechanical treatment of the interaction between an electron and the optical-phonon field of the film. Retardation effects are neglected. The analog of Fröhlich's polaron Hamiltonian is obtained, but with explicit inclusion of surface effects. As a first application of this theory, the case of a fast electron is treated, and the electron-crystal energy-exchange spectra are derived. The classical energy-loss spectrum is recovered and involves processes resulting in one-phonon excitation. Quantum-mechanical two-phonon processes are evaluated. The gain spectrum is obtained for the first time and shows a strong temperature dependence. The results are in good agreement with experimental spectra in LiF crystal films.

I. INTRODUCTION

The study of the interaction between electrons and various elementary excitations of a solid in the neighborhood of a boundary surface is of primary interest for the understanding of a number of phenomena involving surfaces, such as transport properties of thin films, photoemission, electron diffraction, etc.

A particularly clear case of strong surface effects on the electron behavior has been demonstrated by Boersch *et al.*[1] in their measurements of electron energy-loss and -gain spectra in LiF crystal films. Their results show that, for thicknesses up to a few thousand Å, energy exchange between the electron and the crystal film is mainly due to the strong coupling between the electron and the surface-optical phonons, whereas for a thick crystal slab the more efficient coupling is with the usual bulk longitudinal-optical (LO) phonons. A similar coupling has been exhibited recently in LEED and photoemission, in the plasmon energy range.[2] The same pattern is indicated in recent tunneling experiments in semiconductor-metal boundary layers[3] where, again, the electron is strongly coupled to the surface plasmon.[4]

Several authors[5–10] have developed a classical theory to describe the energy-loss spectrum of fast electrons in thin films in both the plasmon and phonon energy ranges. For lower energies where the quantum nature of the electron and the elementary excitation should be taken into account, it would be desirable to set up a Hamiltonian formalism which would properly include surface effects.

In the present paper a quantum-mechanical theory[11] for the interaction electron–long-wavelength optical phonon of a dielectric slab will be developed. It will incorporate explicitly the features of the phonon modes associated with surfaces.

In Sec. II, the classical Hamiltonian of the problem is written using the polarization eigenmodes of the slab already obtained by Fuchs and Kliewer[12]; then (Secs. II and III) the phonon field is quantized in the standard manner, hence obtaining a Hamiltonian similar to Fröhlich's in polaron theory.[13] As far as the coupling to the (LO) phonons is concerned, the only difference from Fröhlich's Hamiltonian is the "space quantization" of the LO modes. More important is the fact that the electron is also coupled to the so-called surface phonons, *although the polarization associated with these modes is divergence free*. These and other features to be discussed may be of considerable importance for the polaron theory in finite-size crystals.[14]

Section IV deals with the case of an electron at rest imbedded in a dielectric. This case corresponds to the calculation of the screening of a fixed charge by the phonon field.

Section V treats the situation where the electron is sufficiently fast for its velocity to remain essentially unaltered by the interaction with the phonon field (yet not fast enough to include relativistic corrections). This case is exactly soluble and provides a suitable quantum-mechanical model for calculating the energy-exchange spectrum in the phonon energy range.

The spectrum which is obtained in the framework of classical electrodynamics[9] is recovered here as resulting from one-phonon processes. Multiphonon processes are evaluated and they are found to give negligible contributions beyond the two-phonon excitation threshold. The gain spectrum is also calculated and shows the observed strong temperature dependence.[1,8]

The quasistatic approximation for the polarization field will be used throughout this paper; no account

of retardation effects is taken care of. These could be included in a more general theory based on the classical treatment of the retarded polarization eigenmodes.[15,16]

II. FREE POLARIZATION IN THE SLAB

A. Integral Equation

The problem of finding the long-wavelength polarization eigenmodes of a dielectric slab of a given uniform dielectric function $\epsilon(\omega)$ can be solved either as a problem of classical electrodynamics by matching boundary conditions, etc., or by incorporating the boundary conditions of the problem into an integral equation for the polarization. Both methods have been used[12,15] for discussing the optical properties of ionic crystals. The integral-equation method will be outlined here, mainly to introduce our notations in a form suitable for the subsequent analyses.

As stated in the Introduction, only the nonretarded equations of motion will be treated. The equation of motion for the displacement fields $\vec{U}_+(\vec{r},t)$ and $\vec{U}_-(\vec{r},t)$ of the (continuous distribution of) positive and negative charges $\pm e_q$, respectively, is

$$\mu[\ddot{\vec{U}}_+(\vec{r},t)-\ddot{\vec{U}}_-(\vec{r},t)]=-\mu\omega_0^2(\vec{U}_+-\vec{U}_-)+e_q\vec{E}(\vec{r},t)\ , \tag{2.1}$$

where μ is the reduced mass of the ion pair, $\mu\omega_0^2$ is a short-range force constant (excluding Coulomb fields), and $\vec{E}(\vec{r},t)$ is the local electric field.[17]

In the dipole approximation, the local field is given by

$$\vec{E}(\vec{r},t)=\vec{E}_L(\vec{r})-\int_{\text{slab}} e_q\vec{\vec{T}}(\vec{r}-\vec{r}')\cdot[\vec{U}_+(\vec{r}',t) - \vec{U}_-(\vec{r}',t)]n\ d\vec{r}', \tag{2.2}$$

where n is the ionic pair density. The integral gives the dipole field propagated by the dipolar tensor T,

$$\vec{\vec{T}}(\vec{r})=(\vec{\vec{E}}-3\vec{r}^0\vec{r}^0)/r^3\ , \tag{2.3}$$

where $\vec{\vec{E}}$ is the unit matrix and the superscript 0 indicates a unit vector. $\vec{E}_L(\vec{r})$ is the Lorentz local-field contribution

$$\vec{E}_L(\vec{r})=\frac{4\pi}{3}\begin{pmatrix}1&0&0\\0&1&0\\0&0&-2\end{pmatrix}\cdot\vec{P}(\vec{r})\ , \tag{2.4}$$

which depends on the polarization $\vec{P}$ at $\vec{r}$. The origin of this term is related to the pathological behavior of dipole lattice sums, as has been discussed at length by de Wette and Schacher.[18] The polarization itself is defined by

$$\vec{P}(\vec{r},t)=ne_q[\vec{U}_+(\vec{r},t)-\vec{U}_-(\vec{r},t)]\ , \tag{2.5}$$

and from (2.1) and (2.2), $\vec{P}(\vec{r})$ satisfies the integral equation

$$\ddot{\vec{P}}(\vec{r},t)+\left[\omega_0^2\vec{\vec{E}}-\frac{4\pi ne_q^2}{\mu}\begin{pmatrix}\frac{1}{3}&0&0\\0&\frac{1}{3}&0\\0&0&-\frac{2}{3}\end{pmatrix}\right]\cdot\vec{P}(\vec{r},t)$$
$$=-ne_q^2/\mu\int_s\vec{\vec{T}}(\vec{r}-\vec{r}')\cdot\vec{P}(\vec{r}',t)\,d\vec{r}'\ . \tag{2.6}$$

Assuming that $\vec{P}(\vec{r},t)=\vec{P}(\vec{r})e^{i\omega t}$, Eq. (2.6) can be written as

$$(\lambda\vec{\vec{E}}-\vec{\vec{\Lambda}})\cdot\vec{P}(\vec{r})=\int_s\vec{\vec{T}}(\vec{r}-\vec{r}')\cdot\vec{P}(\vec{r}')\,d\vec{r}'\ , \tag{2.7}$$

where

$$\lambda=4\pi\omega^2/\omega_p^2\ ,\quad \lambda_0=4\pi\omega_0^2/\omega_p^2\ , \tag{2.8}$$

$$\lambda_T=\lambda_0-\tfrac{4}{3}\pi,\qquad \lambda_L=\lambda_0+\tfrac{8}{3}\pi\ , \tag{2.9}$$

and

$$\vec{\vec{\Lambda}}=\begin{pmatrix}\lambda_T&0&0\\0&\lambda_T&0\\0&0&\lambda_L\end{pmatrix}\ . \tag{2.10}$$

$\lambda_T^{1/2}$ and $\lambda_L^{1/2}$ are the bulk TO and LO frequencies, respectively, in units of the ion plasma frequency

$$\omega_p=(4\pi ne_q^2/\mu)^{1/2}\ .$$

The symmetries of the slab will be used now. First, the translational invariance for continuous displacements parallel to the slab is exploited by introducing two-dimensional Fourier transforms

$$\vec{P}(\vec{r})=A\int d\vec{k}\,e^{i\vec{k}\cdot\vec{\rho}}\vec{P}(\vec{k},z)\ , \tag{2.11}$$

where A is a unit area of the slab surface and $(\vec{\rho},z)$ are the surface and normal components of $\vec{r}$. Since $\vec{P}(\vec{r})$ is real, its Fourier transform must satisfy the following condition:

$$\vec{P}(\vec{k},z)=\vec{P}^*(-\vec{k},z)\ . \tag{2.12}$$

The two-dimensional Fourier transform of $\vec{\vec{T}}(\vec{r}-\vec{r}')$ is derived from

$$1/r=\int d\vec{k}\,e^{i\vec{k}\cdot\vec{\rho}-k|z|}/2\pi k\ . \tag{2.13}$$

By successive differentiations one obtains

$$\vec{r}/r^3=-\int d\vec{k}\,e^{i\vec{k}\cdot\vec{\rho}}(i/2\pi k)\vec{k}e^{-k|z|}\ , \tag{2.14}$$

$$(\vec{\vec{E}} - 3\vec{r}^0\vec{r}^0)/r^3 = \int d\vec{k}\; e^{i\vec{k}\cdot\vec{r}}(1/2\pi k)\vec{\vec{K}}\vec{\vec{K}}\, e^{-k|z|}, \tag{2.15}$$

where

$$\vec{\vec{K}} = [\vec{k}, i\theta(z)k], \quad \theta(z) = +1 \text{ if } z > 0, \quad = -1 \text{ if } z < 0. \tag{2.16}$$

Substituting (2.11) and (2.15) into (2.7), one finds

$$(\lambda\vec{\vec{E}} - \vec{\vec{\Lambda}})\cdot\vec{P}(\vec{k}, z) = (2\pi/k)\int_{-a}^{+a} dz'\, e^{-k|z-z'|}\,\vec{\vec{K}}\vec{\vec{K}}\cdot\vec{P}^*(\vec{k}, z'). \tag{2.17}$$

Next, the rotational invariance round the z axis is exploited. Using the $\vec{k}$ reference frame, the polarization is written

$$\vec{P}(\vec{k}, z) = P(k, z)\vec{k}^0 + P_z(k, z)\vec{z}^0 + P_n(k, z)\vec{n}^0, \tag{2.18}$$

where

$$\vec{n}^0 = \vec{z}^0 \times \vec{k}^0 .$$

This splits Eq. (2.17) into

$$(\lambda - \lambda_T)\, P_n(k, z) = 0 \tag{2.19}$$

and

$$\lambda\vec{\pi}(k, z) = \int_{-a}^{a} dz'\, \vec{\vec{M}}(z - z')\cdot\vec{\pi}(k, z') . \tag{2.20}$$

The $\vec{\pi}(k, z)$ is a two-dimensional polarization vector defined by

$$\vec{\pi}(k, z) = [P(k, z), P_z(k, z)] , \tag{2.21}$$

which, as a consequence of (2.12) and (2.18), must satisfy

$$\vec{\pi}(\vec{k}, z) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \vec{\pi}^*(-\vec{k}, z) .$$

In Eq. (2.20) the kernel $\vec{\vec{M}}$ is given by

$$\vec{\vec{M}}(z - z') = \begin{pmatrix} \lambda_T & 0 \\ 0 & \lambda_L \end{pmatrix} \delta(z - z') + 2\pi k e^{-k|z-z'|} \times \begin{pmatrix} 1 & -i\theta(z - z') \\ i\theta(z - z') & 1 \end{pmatrix} . \tag{2.23}$$

B. Polarization Eigenmodes

The solutions of (2.19) are trivial[12]: Any function of z defined in the interval $(-a, +a)$ satisfies this equation with the degenerate eigenvalue $\lambda = \lambda_T$. An arbitrary pattern of surface polarization may be expanded in terms of a complete set of orthonormalized eigenfunctions in the interval $(-a, +a)$. One can choose, for example,

$$P_{nj+}(z) = i\cos(j\pi/a)z , \tag{2.24}$$

$$P_{nj-}(z) = i\sin(j\pi/a)z , \tag{2.25}$$

where j is a non-negative integer. These transverse modes of vibration (S polarization) are completely decoupled from the P polarization modes and, moreover, they do not interact with the electron, as will be shown later.

Differentiating Eq. (2.20) twice, and, provided that $\det(\lambda\vec{\vec{E}} - \vec{\vec{\Lambda}}) \neq 0$, one obtains the differential equation

$$\frac{d^2}{dz^2}\vec{\pi}(k, z) = k^2\vec{\pi}(k, z) , \tag{2.26}$$

whose solutions are the eigenvectors of the surface polarization waves. If, on the other hand,

$$\det(\lambda\vec{\vec{E}} - \vec{\vec{\Lambda}}) = 0 , \tag{2.27}$$

then Eq. (2.20) is satisfied by the ordinary sine or cosine bulk polarization waves with the important difference that only a discrete set of wave vectors k_z is allowed as a result of the finite thickness of the slab.

Because of the existence of the $z = 0$ plane of mirror symmetry, all the modes can be further classified as even or odd with respect to that symmetry. The detailed analysis is given in Ref. 12. We reproduce the results in Appendix A. The eigenvectors of Eq. (2.20) have been orthonormalized according to

$$\int_{-a}^{+a} dz\, \vec{\pi}^*_{mp}\cdot\vec{\pi}_{m'p'} = \delta_{mm'}\delta_{pp'} . \tag{2.28}$$

They also satisfy the closure relation

$$\sum_{mp} \vec{\pi}^*_{mp}(z)\vec{\pi}_{mp}(z') = \delta(z - z')\vec{\vec{E}} , \tag{2.29}$$

which will be used later on. In Eqs. (2.28) and (2.29) the index m which takes the values $m = 0, 1, 2, \ldots$, has the meaning of a "quantized" wave vector k_z and $p = \pm 1$ is the parity. Both relations result from the Hermitian character of the kernel $\vec{\vec{M}}$ of the integral equation (2.20),

$$\vec{\vec{M}}(z - z') = \vec{\vec{M}}^\dagger(z - z') . \tag{2.30}$$

C. Free-Polarization Hamiltonian

The equation of motion (2.6) of the free polarization field is the Heisenberg evolution equation of the operator $\vec{P}(\vec{r})$,

$$\ddot{\vec{P}}(\vec{r}) = (i/\hbar)[H_p, \vec{P}(\vec{r})], \tag{2.31}$$

if the free polarization Hamiltonian is taken to be

$$H_p = \int_s d\vec{r}\,(2\pi/\omega_p^2)[\vec{P}^2(\vec{r}) + (\omega_p^2/4\pi)\vec{P}(\vec{r})\cdot\vec{\vec{\Lambda}}\cdot\vec{P}(\vec{r}) + \tfrac{1}{2}\int_s d\vec{r}\int_s d\vec{r}'\,\vec{P}(\vec{r})\cdot\vec{\vec{T}}(\vec{r} - \vec{r}')\cdot\vec{P}(\vec{r}') , \tag{2.32}$$

and provided one postulates the commutation relation

$$[\dot{P}_\mu(\vec{r}), P_\nu(\vec{r}')] = (\hbar/i)(\omega_p^2/4\pi)\delta(\vec{r}-\vec{r}')\delta_{\mu\nu} \quad . \quad (2.33)$$

In terms of the Fourier components of $\vec{P}(\vec{r})$ defined in (2.11) these relations become

$$[\dot{P}_\mu(\vec{k}, z), P_\nu(\vec{k}', z')]$$

$$= (\hbar/i)(\omega_p^2/4\pi)(2\pi A)^{-2}\delta(\vec{k}-\vec{k}')\delta(z-z')\delta_{\mu\nu} \quad , \quad (2.34)$$

hence, yielding

$$H_p = (2\pi A)^2 \int d\vec{k}\{\int_{-a}^{+a} dz\,(2\pi/\omega_p^2)[\dot{\vec{P}}^*(\vec{k}, z)\cdot\dot{\vec{P}}(\vec{k}, z)$$

$$+ (\omega_p^2/4\pi)\vec{P}^*(\vec{k}, z)\cdot\vec{\Lambda}\cdot\vec{P}(\vec{k}, z)]$$

$$+ \tfrac{1}{2}\int_{-a}^{+a} dz'\,\vec{P}^*(\vec{k}, z)\cdot[(-2\pi/k)e^{-k|z-z'|}\vec{K}\vec{K}]\cdot\vec{P}(\vec{k}, z')\}. \quad (2.35)$$

Proceeding in the standard manner, the polarization operators $\vec{P}(\vec{k}, z)$ are expanded in terms of a complete set of orthonormal eigenvectors

$$\vec{P}_i(\vec{k}, z) = [\vec{\pi}_{mp}(\vec{k}, z), P_{nj}(\vec{k}, z)] \quad ,$$

where the $\vec{\pi}_{mp}$ and P_{nj} have been defined above:

$$\vec{P}(\vec{k}, z) = \frac{1}{2\pi A^{1/2}}\sum_i \left(\frac{\hbar\omega_p^2}{8\pi\omega_i}\right)^{1/2}(a_i + a_i^\dagger)\vec{P}_i(\vec{k}, z), \quad (2.36)$$

$$\dot{\vec{P}}(\vec{k}, z) = \frac{1}{2\pi A^{1/2}}\sum_i \left(\frac{\hbar\omega_p^2\omega_i}{8\pi}\right)^{1/2} i(a_i^\dagger - a_i)\vec{P}_i(\vec{k}, z) \quad . \quad (2.37)$$

The coefficients of these expansions are the creation and annihilation operators of the corresponding eigenmodes and, from (2.34) and (2.29), they satisfy

$$[a_i(\vec{k}), a_j^\dagger(\vec{k}')] = (1/A)\delta(\vec{k}-\vec{k}')\delta_{ij} \quad . \quad (2.38)$$

Substituting (2.36) and (2.37) into (2.35) yields

$$H_p = H_\pi + H_n \quad , \quad (2.39)$$

where H_n is the completely independent Hamiltonian of the S polarization waves given by the expression

$$H_n = A\int d\vec{k}\sum_{j,p}\hbar\omega_T[a_{njp}^\dagger(\vec{k})a_{njp}(\vec{k}) + \tfrac{1}{2}] \quad , \quad (2.40)$$

and where H_π is the P polarization Hamiltonian

$$H_\pi = A\int d\vec{k}\sum_{mp}\hbar\omega_{mp}(\vec{k})[a_{mp}^\dagger(\vec{k})\,a_{mp}(\vec{k}) + \tfrac{1}{2}] \quad . \quad (2.41)$$

Here the summation extends over all the π eigenmodes listed in Appendix A. All the LO and TO modes are degenerate and only the surface modes have a spatial dispersion.

III. ELECTRON-PHONON INTERACTION

If $\vec{r}_e$ is the position of the electron (charge $-e$), the polarization at $\vec{r}$ sees an additional field

$$\vec{E}_e(\vec{r}) = -\,(\vec{r}-\vec{r}_e)/|\vec{r}-\vec{r}_e|^3 \quad . \quad (3.1)$$

Therefore, the dipolar coupling will result in the following electron-phonon interaction energy:

$$H_I = e\int_s d\vec{r}\,(\vec{r}-\vec{r}_e)/|\vec{r}-\vec{r}_e|^3\cdot\vec{P}(\vec{r}) \quad . \quad (3.2)$$

Using the Fourier expansions (2.11) and (2.14), this transforms into

$$H_I = (2\pi A)e\int d\vec{k}\,e^{-i\vec{k}\cdot\vec{\rho}_e}$$

$$\times\int_{-a}^{a} dz\,e^{-k|z-z_e|}(i/k)\vec{K}\cdot\vec{P}^*(\vec{k}, z) \quad . \quad (3.3)$$

From this expression, and due to the particular form [Eq. (2.16)] of the vector $\vec{K}$, it is immediately apparent that the electron couples only to the P polarization and not to the completely transverse S polarization P_n. Finally, use of second quantization yields

$$H_I = A\int d\vec{k}\,e^{-i\vec{k}\cdot\vec{\rho}_e}\sum_i \Gamma_i(k, z_e)(a_i^\dagger + a_i), \quad (3.4)$$

where the coupling functions Γ_i are defined by

$$\Gamma_i(k, z_e) = (\hbar e^2\omega_p^2/8\pi A\omega_i)^{1/2}\int_{-a}^{a} dz\,e^{-k|z-z_e|}\vec{\chi}\cdot\vec{\pi}_i^*(z), \quad (3.5)$$

where

$$\vec{\chi} = [i, -\theta(z-z_e)]. \quad (3.6)$$

Inserting in (3.5) the various eigenvectors of Appendix A, one is left with elementary quadratures to obtain the explicit form of the coupling functions Γ_i. These functions are listed in Appendix B. It turns out that the electron does not couple to the TO modes of P polarization any more than to the S polarization waves. As for the case of an infinite dielectric medium, this can be seen to result essentially from the fact that the polarization field associated with any TO mode is divergence free. Indeed,

$$\operatorname{div}\vec{P}(\vec{r}) = \int d\vec{k}\,e^{i\vec{k}\cdot\vec{\rho}}\left(i\vec{k}, \frac{\partial}{\partial z}\right)\cdot\vec{P}(\vec{k}, z), \quad (3.7)$$

$$\operatorname{div}\vec{P}(\vec{r}) = \int d\vec{k}\,e^{i\vec{k}\cdot\vec{\rho}}\left(ikP + \frac{\partial P_z}{\partial z}\right), \quad (3.8)$$

and the integrand is identically zero for the TO modes. The z_e dependence of the various coupling functions $\Gamma_i(k, z_e)$ is sketched in Fig. 1.

Comparing the maximum strengths of the surface and LO coupling functions, one finds (see Appendix B)

$$\max(\Gamma^{L}_{m\pm}) = g_m 2\left(\frac{a}{k^2a^2+\frac{1}{4}m^2\pi^2}\right)^{1/2} \leq \frac{4}{\pi}\,(\sqrt{a})\,g_m, \tag{3.9}$$

$$\max(\Gamma_{0\pm}) = g_0(\sinh 2ka/k)^{1/2}e^{-ka} \leq (\sqrt{2a})g_0. \tag{3.10}$$

Noting that $g_0 \simeq g_m$, we see that the surface modes, *in spite of their divergence-free character*, are coupled to the electron just as strongly as any LO mode. One could argue that due to the larger number of LO modes for each $\vec{k}$ in a relatively thick slab, [19] the surface effects studied here on the electron properties will be negligible. However, this is certainly not the case for properties which depend on a selective and particular phonon frequency (such as the electron energy-loss or -gain spectra considered below). In fact, two features, peculiar to the surface vibrations, may be of great importance in the behavior of the electron close to the surface. First, there is a continuum of surface state energies available for transitions between ω_T and ω_L, whereas in the bulk only a sharp state round ω_L is coupled to the electron. Second, the surface coupling function dies off as $k^{-1/2}$ for large k [Eq. (3.10)], whereas the LO coupling function goes as k^{-1} [Eq. (3.9); this is well known in Fröhlich's Hamiltonian].[13] Therefore, for the case of conduction electrons in a polar dielectric slab thinner than, say, 5000 Å, it does not seem justifiable to neglect the surface effects associated with the existence of these surface phonons. The application of various techniques of the theory of large polaron to the present Hamiltonian is being carried out. [14]

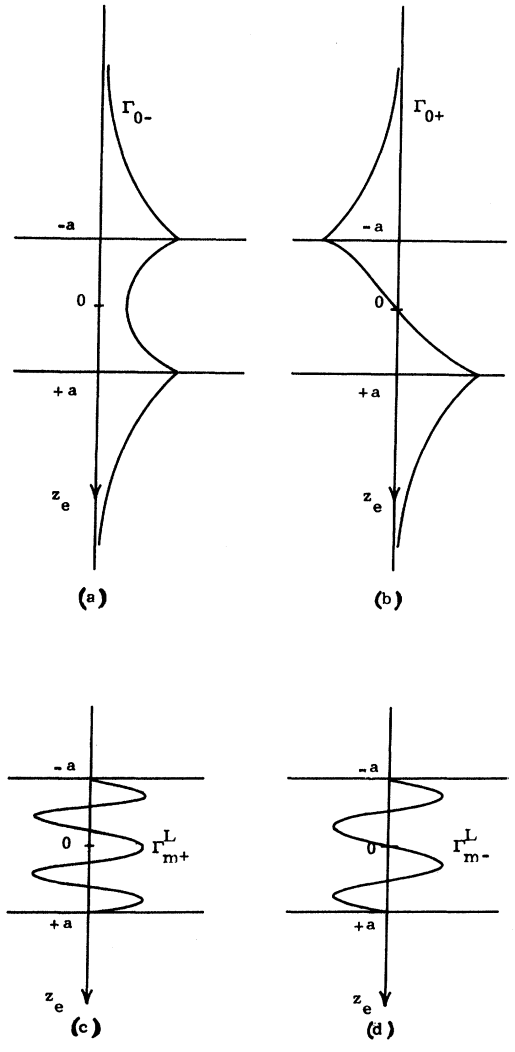

FIG. 1. Spatial dependence of the coupling functions $\Gamma_i(k, z_e)$. (a) and (b) give the coupling strength for the two surface modes. (c) and (d) correspond to the LO modes. The TO modes are not coupled to the electron (see Appendix B).

IV. SCREENING OF A FIXED CHARGE

As a first simple application of Hamiltonian (2.41), (3.4), the screening of a perfectly localized point charge provided by the phonon field will be considered. For this case, the coupling functions $\Gamma_i(k, z_e)$ are constant. The phonon field operators are then statically displaced (assuming $\vec{\rho}_e = \vec{0}$):

$$\alpha_i = a_i + \Gamma_i/\hbar\omega_i. \tag{4.1}$$

This yields a Hamiltonian diagonal in α_i,

$$H = A\int d\vec{k}\sum_i [\hbar\omega_i(\alpha_i^\dagger\,\alpha_i + \tfrac{1}{2}) - \Gamma_i^2/\hbar\omega_i]. \tag{4.2}$$

The second term of (4.2),

$$E_S = -A\int d\vec{k}\sum_i \Gamma_i^2/\hbar\omega_i\ , \tag{4.3}$$

gives the infinite classical self-energy of the electron in the polarization field it induces. As an illustration, the ground-state average polarization[20] at the center of the slab due to a point charge at the surface $z_e = +a$ will be computed. Using (2.11), (2.36), and (4.1), one finds

$$\langle \vec{P}(\vec{r}=0)\rangle = (\sqrt{A}\left(\frac{\hbar\omega_p^2}{8\pi}\right)^{1/2}\int k\,dk\sum_i \frac{1}{\sqrt{\omega_i}} \times \langle a_i + a_i^\dagger\rangle\,\vec{P}_i(\vec{k},0) \tag{4.4}$$

$$= -2(\sqrt{A}\,)\left(\frac{\hbar\omega_p^2}{8\pi}\right)^{1/2}\int k\,dk \times\sum_i \frac{\Gamma_i(\vec{k},a)}{(\sqrt{\omega_i})\hbar\omega_i}\,\vec{P}_i(\vec{k},0)\ . \tag{4.5}$$

The z component of $\vec{P}$ will receive contributions

only from the (0_+) surface mode; that is,

$$\langle P_z(0)\rangle = (e/2\pi)\int_0^\infty k\,dk\,e^{-ka}/(\beta+e^{-2ka}) \ , \quad (4.6)$$

where

$$\beta = 2\omega_T^2/\omega_p^2 + 1 \ . \quad (4.7)$$

This result can also be derived from classical electrostatics or, equivalently, by solving the inhomogeneous integral equation obtained by setting $\lambda = 0$ in Eq. (2.20) and by adding a source term $\vec{\pi}_0$ due to the point charge

$$\int_{-a}^{+a} dz'\,\vec{\vec{M}}(z-z')\cdot\vec{\pi}(\vec{k},z') = \vec{\pi}_0 \ , \quad (4.8)$$

with

$$\vec{\pi}_0 = (ie/2\pi A)\,e^{-k|z-z_e|}\,[1, i\theta(z-z_e)] \ . \quad (4.9)$$

Equation (4.8) is solved by expressing $\vec{\pi}$ in terms of the complete set of eigenvectors $\vec{\pi}_i(z)$:

$$\vec{\pi}(z) = \sum_i \left[\frac{1}{\lambda_i}\int_{-a}^{a} dz'\,\vec{\pi}_0(z')\cdot\vec{\pi}_i^*(z')\right]\vec{\pi}_i(z) \ . \quad (4.10)$$

The factor in square brackets essentially gives Γ_i [see Eq. (3.5)]. Therefore, (4.10) is equivalent to (4.5).

V. FAST-ELECTRON CASE

A. Evolution of Phonon States

Here it will be assumed that the electron is so fast that any momentum transfer $\hbar\vec{k}$ to the phonon field is much smaller than the electron momentum $p = \sqrt{2mE_0}$, where E_0 is the (essentially constant) electron energy. Then the electron can be treated as a classical particle of constant velocity v and as the source of a time-dependent perturbation of the slab. In the continuum approximation, an upper bound for one-phonon momentum transfer may be $\hbar k \approx 5\times10^{-21}$ g cm/sec (corresponding to a wavelength of ~100 Å). Therefore, for one-phonon processes, the constant-velocity approximation may hold for electron momenta higher than $p \sim 20\hbar\vec{k} \sim 10^{-19}$ g cm/sec, i.e., for energies higher than $p^2/2m \approx 10$ eV.

Setting

$$\vec{\rho}_e = \vec{0}, \quad z_e = vt \ , \quad (5.1)$$

the Hamiltonian (2.41) and (3.4) takes the form

$$H = A\int d\vec{k}\sum_{mp}\left[\hbar\omega_{mp}\left(a_{mp}^\dagger a_{mp}+\tfrac{1}{2}\right)+\Gamma_{mp}(t)\left(a_{mp}^\dagger + a_{mp}\right)\right] \ . \quad (5.2)$$

Consider a particular $(\vec{k}, mp)$ phonon mode with the Hamiltonian

$$h = \hbar\omega\left(a^\dagger a+\tfrac{1}{2}\right)+\Gamma(t)\left(a^\dagger + a\right) \ , \quad (5.3)$$

then, the phonon state vector in the interaction representation

$$|\psi^I(t)\rangle = e^{i\omega(a^\dagger a+1/2)t}\,|\psi^S(t)\rangle \quad (5.4)$$

satisfies the evolution equation[21]

$$i\hbar\frac{d}{dt}|\psi^I(t)\rangle = \Gamma(t)(a^\dagger e^{i\omega t}+ae^{-i\omega t})|\psi^I(t)\rangle \ . \quad (5.5)$$

On integration,

$$|\psi^I(t)\rangle = \exp\left[-(i/\hbar)\int_{t_0}^{t} dt'\,\Gamma(t')\right.$$
$$\left.\times(e^{i\omega t'}a^\dagger + e^{-i\omega t'}a)\right]|\psi^I(t_0)\rangle \ . \quad (5.6)$$

The Γ functions of the present problem have a definite parity p, so that by letting $t_0 \to -\infty$ and $t \to \infty$ and defining

$$I = \int_{-\infty}^{\infty}\Gamma(t)e^{-i\omega t}\,dt \ , \quad (5.7)$$

one has

$$|\psi^I(+\infty)\rangle = e^{-(i/\hbar)I(pa^\dagger + a)}\,|\psi^I(-\infty)\rangle \quad (5.8)$$

or

$$|\psi^I(+\infty)\rangle = e^{-(1/2)pI^2/\hbar^2}e^{-(i/\hbar)Ipa^\dagger}e^{-(i/\hbar)Ia}\,|\psi^I(-\infty)\rangle \ . \quad (5.9)$$

Let $|n^0\rangle$ represent the initial state of excitation of the phonon mode; then one finds, on expanding the exponential operators,

$$|\psi_{n^0}^I(+\infty)\rangle = e^{-(1/2)pI^2/\hbar^2}\sum_{m=0}^{\infty}\sum_{n=0}^{n^0}\frac{[n^0!\,(n^0-n+m)!]^{1/2}}{m!\,n!\,(n^0-n)!}$$
$$\times\left(-i\frac{I}{\hbar}\right)^{n+m}p^m|n^0-n+m\rangle \ . \quad (5.10)$$

To carry out the sum, the summation order is changed such that

$$m = n+r > 0 \ , \quad m+n > 0 \ , \quad (5.11)$$

hence,

$$|\psi_{n^0}^I(+\infty)\rangle = \sum_{r=-n^0}^{\infty} C_{n^0 r}\,|n^0+r\rangle \ , \quad (5.12)$$

where

$$C_{n^0 r} = e^{-(1/2)pI^2/\hbar^2}\left(\sum_{n\geq -r/2}^{n^0}\frac{[n^0!\,(n^0+r)!]^{1/2}}{(n+r)!\,n!\,(n^0-n)!}\right.$$
$$\left.\times(-iI/\hbar)^{2n+r}p^{r+n}\right) \quad (5.13)$$

is the probability amplitude of finding the phonon mode in its $|n^0+r\rangle$ excited state when the electron has traveled through the slab.

The total state vector of the slab at $t = +\infty$ is given by

$$|\psi_{\{n^0\}}^I(+\infty)\rangle = \prod_i\left(\sum_{r_i=-n_i^0}^{\infty} C_{n_i^0 r_i}\,|n_i^0+r_i\rangle\right) \ , \quad (5.14)$$

where i stands for $(\vec{k},m,p)$. Equation (5.14) can be rewritten

$$|\psi^{I}_{\{n^0\}}(+\infty)\rangle = \sum_{\{r\}} C_{\{n^0,r\}} |\{n^0+r\}\rangle , \tag{5.15}$$

where

$$C_{\{n^0,r\}} = \prod_i C^0_{n_i,r_i} , \tag{5.16}$$

and

$$|\{n^0+r\}\rangle = \prod_i |n^0_i + r_i\rangle \tag{5.17}$$

is an eigenstate of the Hamiltonian, with a total energy

$$E_{\{n^0,r\}} = \sum_i \hbar\omega_i(n^0_i + r_i + \tfrac{1}{2}) . \tag{5.18}$$

In (5.15), $\sum_{\{r\}}$ means a multiple integration (index $\vec{k}$) and summation (indices m,p) over all the eigenmodes of the slab and over all their possible excitations r.

B. Loss and Gain Spectra: One-Phonon Processes

The coefficients $|C_{\{n^0,r\}}|^2$ of Eq. (5.15) give the probability of finding the phonon field in the eigenstate $|\{n^0+r\}\rangle$ of total energy $E_{\{n^0+r\}}$ at $t=+\infty$, knowing that before the electron passage, i.e., at $t=-\infty$, the phonon field was in $|\{n^0\}\rangle$ eigenstate and characterized by an energy $E_{\{n^0\}}$. Therefore, these coefficients would also give the probability for the electron to exchange energy $E_{\{n^0+r\}} - E_{\{n^0\}} = \pm\hbar\omega$ with the slab. Depending on the sign of this energy difference, one obtains by definition the loss or gain spectrum, respectively.

The initial state of the slab is determined by the Boltzmann statistical factor $Z^{-1}(T)\exp(-E_{\{n^0\}}/kT)$ which gives the probability of finding the phonon field in the $E_{\{n^0\}}$ energy state, in a statistical ensemble at temperature T(Z is the partition function of the phonon field). Thus, the observed energy-exchange spectrum is proportional to the product of the quantum-mechanical probability $|C_{\{n^0,r\}}|^2$ by the statistical factor

$$P(\pm\hbar\omega) = \sum_{\{n^0,r\}} |C_{\{n^0,r\}}|^2 \frac{\exp(-E_{\{n^0\}}/kT)}{Z(T)} \times \delta(\omega \mp \sum_i \omega_i r_i), \tag{5.19}$$

where the δ function takes care of the energy conservation and where the upper and lower signs refer, respectively, to the loss and gain phenomena.

Except for the temperature factor, Eq. (5.19) is Fermi's Golden Rule for the transition probability between two states of energy $E_{\{n^0\}}$ and $E_{\{n^0\}} \pm \hbar\omega$. In the context of this work, this relation provides the exact result, since the interaction causing the transition is linear in the phonon field operators.

The loss spectrum [upper sign in (5.19)] will be examined first. It is clear that the contributions to $P(\hbar\omega)$ can be classified as due to one-, two-, or multi-phonon processes. This can be seen by comparing the value of $\hbar\omega$ to the minimum energy loss, i.e., $\hbar\omega_T$. For $\hbar\omega_T < \hbar\omega < 2\hbar\omega_T$, energy conservation requirement allows excitation involving one phonon only. For $2\hbar\omega_T < \hbar\omega < 3\hbar\omega_T$, two-phonon processes may occur as well, and so on. When the temperature-dependent factor is taken into account, the leading term in the summation over the initial states clearly comes from the ground state of the polarization field in which no phonons are excited: $E_{\{0\}} = \frac{1}{2}\sum_i \hbar\omega_i$. At sufficiently low temperature this leading term is essentially temperature independent as a result of

$$\lim_{kT \ll \hbar\omega_T} Z(T) \simeq e^{-E_{\{0\}}/kT} . \tag{5.20}$$

Hence, in the whole temperature range where one has $kT < \hbar\omega_T$, the loss spectrum will not be very sensitive to changes in the temperature. This is the case for LiF and other alkali-halide crystals for which $\hbar\omega_T \sim 0.05$ eV (~ 600 °K). The next term in the summation (5.19) over initial states would have the extra temperature factor $\exp(-\hbar\omega/kT) \approx 0.1$ at room temperature and therefore may be neglected in first approximation. Therefore, in the case of one-phonon processes and when the slight temperature effects just discussed are neglected, the normalized loss spectrum reduces to one term.

$$P(+\hbar\omega) = P_0 A \int d\vec{k}\, (|I_{mp}(k)|^2/\hbar^2)\,\delta[\omega - \omega_{mp}(\vec{k})], \tag{5.21}$$

where

$$P_0 = \exp(-\textstyle\sum_i p_i I_i^2/\hbar^2) \tag{5.22}$$

is the strength of the no-loss peak which has been subtracted from (5.19). The indices $(\vec{k},m,p)$ of the excited mode are specified by the energy conservation requirement. Five possible values of $P(\hbar\omega)$ may be obtained, depending on the ranges of value of ω.

1. $\omega \leqslant \omega_T$: $P(\hbar\omega) = 0$ (below the threshold of one-phonon excitation).

2. $\omega_T < \omega < \omega_I$: where $\omega_I = [(\epsilon_0+1)/(\epsilon_\infty+1)]^{1/2}$ is the limiting surface mode frequency for large k. In this range, the δ function of (5.21) selects the ω_{0-} mode as the only possible excited mode. Introducing in (5.21) the expression for $I_{0-}(\vec{k})$ given in Appendix B, one finds (dropping the constant exponential factor P_0)

$$P(\hbar\omega) = \frac{\omega_p^2 e^2}{2\hbar v^2} \int_0^\infty dk\, \frac{k^2 \cos^2(\omega_{0-}a/v)}{(k^2+\omega_{0-}^2/v^2)^2\omega_{0-}} \times \tanh ka \left(\left|\frac{\partial\omega_{0-}}{\partial k}\right|\right)^{-1} \delta(k-k_-), \tag{5.23}$$

where k_- is the zero of $\omega - \omega_{0-}(k)$ and can be found explicitly from the dispersion relation (see Appendix A)

$$\omega_{0-} = [\omega_T^2 + \tfrac{1}{2}\omega_p^2(1 - e^{-2ka})]^{1/2} . \quad (5.24)$$

This can be rewritten as

$$(\epsilon - 1)/(\epsilon + 1) = e^{2ka} \quad \text{or} \quad -1/\epsilon = \tanh ka , \quad (5.25)$$

where

$$\epsilon(\omega) = (\omega_L^2 - \omega^2)/(\omega_T^2 - \omega^2) \quad (5.26)$$

is the dielectric constant of the infinite medium at frequency ω.

To calculate $|\partial\omega_{0-}/\partial k|$, Eqs. (5.24) and (5.25) are used, and this leads to

$$P(\hbar\omega) = \frac{4e^2}{\hbar v^2} \frac{L^{-1}k_-^2}{(k_-^2 + \omega_-^2/v^2)^2} \frac{1-\epsilon}{\epsilon(1+\epsilon)} \cos^2\frac{\omega_- a}{v} , \quad (5.27)$$

which is the result obtained by Lucas and Karheuser[9] through classical electrodynamics.

3. $\omega_I < \omega < \omega_L$: The δ function of (5.23) selects here the ω_{0+} mode. One finds for this case

$$P(\hbar\omega) = \frac{4e^2}{\hbar v^2} \frac{L^{-1}k_+^2}{(k_+^2 + \omega_+^2/v^2)^2} \frac{\epsilon - 1}{\epsilon(\epsilon+1)} \sin^2\frac{\omega_+ a}{v} . \quad (5.28)$$

4. $\omega > \omega_L$: $P(\hbar\omega) = 0$ since one-phonon processes cannot contribute here.

5. $\omega = \omega_L$: Since all the longitudinal modes are degenerate at that frequency, the probability for the electron to lose the energy $\hbar\omega_L$ will be the sum of the independent probabilities arising from each mode:

$$P(\hbar\omega_L) = A \int d\vec{k} \left(\sum_{m \text{ even}} \frac{|I^L_{m-}|^2}{\hbar^2} + \sum_{m \text{ odd}} \frac{|I^L_{m+}|^2}{\hbar^2} \right) \delta(\omega - \omega_L) . \quad (5.29)$$

To evaluate (5.29), the expressions for $I^L_{m\pm}$ given in Appendix B can be introduced and summed term by term. However, a simpler way to get the result in closed form is to use the closure relation (2.29) for the eigenvectors: Setting $i \equiv (mp)$, then, for any $\vec{k}$,

$$\sum_i |I_i^L(k)|^2 = (g^2/A\omega_L) \int_{-\infty}^{+\infty} \int dt\, dt'\, e^{-i\omega_L(t-t')} \cdot \int_{-a}^{a}\int_{-a}^{a} dz\, dz'\, e^{-k(|z-z_e|+|z'-z'_e|)} \vec{\chi}(z - z_e) \cdot [\textstyle\sum_i \vec{\pi}_i^L{}^*(z)\vec{\pi}_i^L(z')] \cdot \vec{\chi}(z' - z'_e) , \quad (5.30)$$

where

$$g = (\hbar e^2\omega_p^2/8\pi)^{1/2} . \quad (5.31)$$

To the sum $\sum_i$ of the right-hand side of the above equation, one may add the tensor $\sum_i \vec{\pi}_i^T{}^*(z)\vec{\pi}_i^T(z')$. This merely introduces the coupling functions Γ_i^T of the transverse modes which are known to be identically zero. Using, now, the closure relation (2.29),

$$\sum_i [\vec{\pi}_i^L{}^*(z)\vec{\pi}_i^L(z') + \vec{\pi}_i^T{}^*(z)\vec{\pi}_i^T(z')] = \delta(z - z')\vec{\vec{E}} - \sum_{p=\pm1} \vec{\pi}^*_{0p}(z)\vec{\pi}_{0p}(z') . \quad (5.32)$$

On substituting (5.32) in (5.30) one obtains

$$\sum_i |I_i^L(k)|^2 = \frac{g^2}{A\omega_L} \int_{-a}^{a} dz \left| \int_{-\infty}^{+\infty} dt\, e^{-i\omega_L t - k|z-z_e|} \vec{\chi}(z - z_e) \right|^2 - \sum_{p=\pm1} \frac{\omega_{0p}}{\omega_L} \left| \int_{-\infty}^{\infty} dt\, e^{-i\omega_L t} \Gamma_{0p}(t) \right|^2 , \quad (5.33)$$

which in fact leads to trivial integrations already met in the evaluation of I_{0p}. The final result is

$$\sum_i |I_i^L(k)|^2 = \frac{C}{(k^2 + \omega_L^2/v^2)} - \sum_{p=\pm1} |I_{0p}(\omega_L)|^2 , \quad (5.34)$$

where

$$C = (e^2 a\omega_p/\pi v^2)\hbar . \quad (5.35)$$

Integrating (5.34) with respect to $\vec{k}$ yields

$$P(\hbar\omega_L) = \frac{e^2 a}{\hbar v^2} \ln\left(\frac{k_c^2 + \omega^2/v^2}{\omega^2/v^2}\right)\omega_p\, \delta(\omega - \omega_L) - \frac{2\hbar\omega_p^2 e^2}{\omega_L v^2} \times \int_0^{k_c} dk \frac{k^2}{(k^2 + \omega_L^2/v^2)^2} \left(\tanh ka \cos^2\frac{\omega_L a}{v} + \frac{1}{\tanh ka} \sin^2\frac{\omega_L a}{v} \right) \delta(\omega - \omega_L) , \quad (5.36)$$

where k_c is a cutoff wave vector related to the aperture of the electron spectrometer.[1,9]

The first term in (5.36) gives the bulk loss contribution at ω_L obtained in the classical theory.[7,9] The second term of (5.36) gives the so-called "Begrenzung" effect,[8] i.e., a reduction of the strength of the resonant bulk loss at ω_L. The origin of this term is particularly clear in the present formalism: The closure relation (5.32) expresses a sum rule according to which part of the total density of states has been removed from the δ singularity at ω_L and has gone into the two surface phonon states. Therefore, in the limit of very small slab thickness, it is obvious that the Begrenzung term should ultimately cancel the resonant bulk loss. This compensation can easily be checked by expanding the integrand of (5.36) in powers of ka. It plays an important role, even for thicknesses up

to a few thousand Å.

The gain spectrum is evaluated in a similar fashion. From (5.19) one sees that any nonvanishing term in the summation must involve some excitation of the phonon field in the initial state of the slab. This initial excitation can then be transferred to the passing electron. As for the previous case, at room temperature, the main contribution will be due to the initial states involving a minimum number of excitations. Hence, the leading term in (5.19) will correspond to the mode $(\vec{k}, m, p)$ being in the initial state $n^0_{mp}(\vec{k}) = 1$ and returning to its ground state with the transfer of one quantum of energy $\hbar\omega_{mp}(k) = \hbar\omega$ to the electron. Using the approximation (5.20) and neglecting multiphonon processes, the gain spectrum may be written as

$$P(-\hbar\omega) = P_0 A \int d\vec{k}\, e^{-\hbar\omega_{mp}(k)/kT}\left(|I_{mp}(k)|^2/\hbar^2\right) \times \delta[\omega - \omega_{mp}(k)] \ . \tag{5.37}$$

Comparing this result with expression (5.21), one finds that, to lowest order in temperature effects, the gain spectrum will be the mirror image of the loss spectrum multiplied by the weight factor $\exp(-\hbar\omega/kT)$. In addition to giving an over-all reduction of the order of $e^{-2} \simeq 0.1$ at room temperature, this temperature factor will have the effect of smoothing out the high-energy features of the loss spectrum, such as the resonant peak at ω_L. However, the gain spectrum is sensitive to small variations in temperature since it depends directly on the initial thermal population of the excited states of the phonon field. The spectra described by Eqs. (5.27), (5.28), (5.36), and (5.37) are sketched in Fig. 2. To conclude this section, it must be pointed out that in the present theory no account is taken of the damping of the phonon modes due to either anharmonicity or radiation damping (retardation effect, see Ref. 15). A small anharmonicity amounts to the inclusion of a small imaginary part in the dielectric constant and its effect is to smooth out somewhat any sharp feature of the spectrum. Concerning radiation damping, recent calculations[9,10] have shown that this and other retardation effects can be neglected.

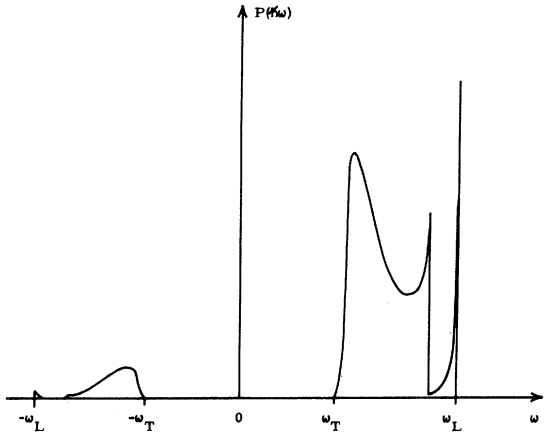

FIG. 2. Electron energy-exchange spectrum in LiF as calculated from Eqs. (5.27), (5.28), (5.36), and (5.37). The gain spectrum corresponds to room temperature.

C. Multiphonon Processes

Finally, the relative importance of multiphonon processes on the loss spectrum will be evaluated; the region studied is restricted to $2\hbar\omega_T < \hbar\omega < \hbar\omega_T$, i.e., between the thresholds of two- and three-phonon losses. In LiF, this energy range includes the LO phonon excitation energy $\hbar\omega_L$ and it should be interesting to compare this purely quantum-mechanical two-phonon loss to the classical contributions studied so far.

According to Eq. (5.19) (upper sign), and if the temperature factor is neglected, the two-phonon loss spectrum is

$$P_2(\hbar\omega) = P_0 A^2 \int\int d\vec{k}\, d\vec{k}' \left|(-iI_{mp}(k)/\hbar)(-iI_{m'p'}(k')/\hbar)\right|^2 \cdot \delta[\omega - (\omega_{mp}(k) + \omega_{m'p'}(k'))] \ . \tag{5.38}$$

Only the energy region close to $\hbar\omega_L$ (see Fig. 3) will be investigated, where the only possible two-phonon process is through the excitation of two low-energy surface modes $\omega_{0-}(k)$. This is sufficient since, beyond ω_L, the experimental spectrum dies off quickly.

Using the δ-function condition one can define a function $K(k, \omega)$, such that

$$\omega = \omega_{0-}(k) + \omega_{0-}(K) \ . \tag{5.39}$$

Equation (5.38) may then be rewritten (dropping the normalization factor P_0)

$$P_2(\hbar\omega) = \frac{4\pi^2 g^4}{\hbar^4 v^4} \int\int dk\, dk'\, F(k)F(k') \times \left|\frac{\partial\omega_{0-}(k)}{\partial k}\right|^{-1}_{k=K} \delta(k' - K) \ , \tag{5.40}$$

where

$$F(k) = \frac{2k^2 \tanh ka \cos^2(\omega_{0-}(k)a/v)}{[k^2 + \omega^2_{0-}(k)/v^2]^2 \omega_{0-}(k)} \ . \tag{5.41}$$

The range of integration over k in (5.40) is from $k = 0$ to a maximum value $\hat{k}$ determined by the relation

$$\omega = 2\omega_{0-}(\hat{k}) \tag{5.42}$$

(see Fig. 3); therefore,

$$P_2(\hbar\omega)=\frac{4\pi^2 g^4}{\hbar^4 v^4}\int_0^{\hat{k}} dk\, F(k)F[K(k,\omega)]\left|\frac{\partial\omega_{0-}(K)}{\partial K}\right|^{-1}. \tag{5.43}$$

In LiF, for $\omega\approx\omega_L$, $\hat{k}$ defined by (5.42) is very small ($\hat{k}_a\approx 0.02$) and hence the integrand can be expanded in powers of ka. Starting from the dispersion relation (A5) one has

$$\omega_{0-}\simeq\omega_T[1+\tfrac{1}{2}(\epsilon_0-\epsilon_\infty)ka]. \tag{5.44}$$

Hence, from (5.39), (5.42), and (5.43) one can write

$$K=2\hat{k}-k, \tag{5.45}$$

$$\hat{k}=(\omega-2\omega_T)/[a\omega_T(\epsilon_0-\epsilon_\infty)], \tag{5.46}$$

and

$$P_2(\hbar\omega)\approx\frac{4\pi^2 g^2}{\hbar^2 v^4}\frac{8a}{\omega_T^3(\epsilon_0-\epsilon_\infty)}\int_0^{\hat{k}} dk\frac{k^3}{(k^2+\omega_T^2/v^2)^2}\cdot\frac{(2\hat{k}-k)^3}{[(2\hat{k}-k)^2+\omega_T^2/v^2]^2}. \tag{5.47}$$

This result can be compared to the maximum loss due to one-surface phonon excitation as given by Eq. (5.23) (see Ref. 9):

$$P_1(\hbar\omega_{\mathrm{Max}})\simeq\frac{2\pi g^2}{\hbar^2 v^2}\frac{4}{\omega_T^2(\epsilon_0-\epsilon_\infty)}\frac{k_M^2}{(k_M^2+\omega_T^2/v^2)^2}, \tag{5.48}$$

where

$$k_M=\sqrt{3}\omega_I/v. \tag{5.49}$$

A typical numerical example appropriate to the experiments on LiF[1] will be considered:

$$\epsilon_0=9.27,\quad \epsilon_\infty=1.92,\quad \omega_T=5.78\times10^{13}\ \mathrm{sec}^{-1},$$

$$v=10^{10}\ \mathrm{cm/sec},\qquad e=e_q=4.8\times10^{-10}\ \mathrm{cgs},$$

$$n=0.05\times10^{24}\ \mathrm{cm}^{-3}.$$

These lead to

$$P_1(\hbar\omega_{\max})\simeq 2\times10^{14}\ \mathrm{sec}. \tag{5.50}$$

For a slab of thickness, say, 500 Å, one has

$$2\hat{k}\approx k_M=10^4\ \mathrm{cm}^{-1}. \tag{5.51}$$

Hence, the second factor of the integrand in (5.47) is a decreasing function of k. Replacing this function by its maximum value, one obtains the upper bound

$$P_2(\hbar\omega_L)/P_1(\hbar\omega_M)\lesssim\frac{2\pi g^2}{\hbar^2 v^2}\frac{2a}{\omega_T}\cdot I(\hat{k}), \tag{5.52}$$

where

$$I(\hat{k})=\int_0^{\hat{k}} dk\frac{k^3}{(k^2+\omega_T^2/v^2)^2}=\tfrac{1}{2}\left[\ln\left(1+\frac{\hat{k}^2v^2}{\omega_T^2}\right)+\left(1+\frac{\hat{k}^2v^2}{\omega_T^2}\right)^{-1}-1\right] \tag{5.53}$$

leading to

$$P_2(\hbar\omega_L)/P_1(\hbar\omega_M)\lesssim 10^{-3}. \tag{5.54}$$

This estimate shows that the two-phonon excitation probability, and certainly higher-order processes, cannot modify significantly the loss spectrum due to one-phonon processes.

VI. CONCLUSIONS

The interaction between an electron and the optical polarization of a homogeneous crystal slab has been studied in the long-wavelength limit (continuum approximation), neglecting retardation. The quantum-mechanical Hamiltonian of the system is obtained.

The electron interacts with the LO phonon modes in the same way as in the infinite crystal (Fröhlich's Hamiltonian[13]). It also couples, with comparable strength, to the surface modes of vibration, although the polarization associated with these modes is divergence free. This latter coupling is likely to play an important role in determining the transport properties of thin films of polar semiconductors or the surface conductivity of thick samples. It might also lead to a new kind of surface state (polaron bound state).

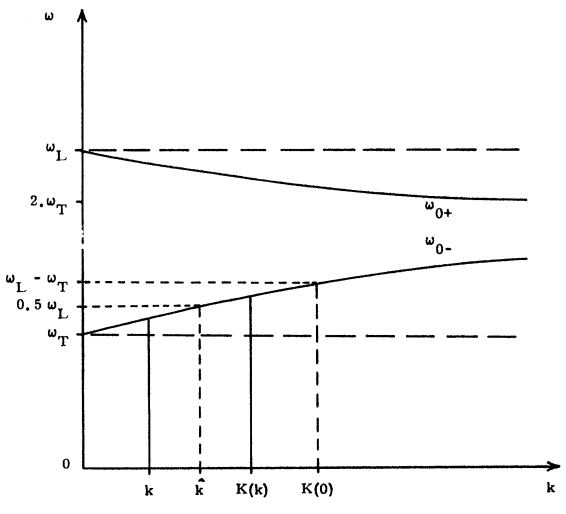

FIG. 3. Range of k integration for two-phonon excitation processes. When k varies from 0 to $\hat{k}$ defined in (5.42), the function $K(k)$ given by (5.39) decreases from $\hat{k}\simeq 2\hat{k}$ to $\hat{k}$. Here the two-phonon excitation probability is evaluated for $\omega\simeq\omega_L$.

TABLE I. Eigenmodes of the P polarization. Because of relation (2.22), the first eigenvector components are pure imaginary and the second are real.

Eigenvalues λ	Eigenvectors $\vec{\pi}$	m
λ_-	$\vec{\pi}_{0-} = C_0\,(i\cosh kz,\ \sinh kz)$	0
λ_+	$\vec{\pi}_{0+} = C_0\,(i\sinh kz,\ \cosh kz)$	0
λ_L	$\vec{\pi}^L_{m-} = C_m\left(ika\sin\frac{m\pi}{2a}z,\ \frac{m\pi}{2}\cos\frac{m\pi}{2a}z\right)$	2, 4, 6, ...
λ_L	$\vec{\pi}^L_{m+} = C_m\left(ika\cos\frac{m\pi}{2a}z,\ -\frac{m\pi}{2}\sin\frac{m\pi}{2a}z\right)$	1, 3, 5, ...
λ_T	$\vec{\pi}^T_{m-} = C_m\left(\frac{im\pi}{2}\cos\frac{m\pi}{2a}z,\ ka\sin\frac{m\pi}{2a}z\right)$	2, 4, 6, ...
λ_T	$\vec{\pi}^T_{m+} = C_m\left(-\frac{im\pi}{2}\sin\frac{m\pi}{2a}z,\ ka\cos\frac{m\pi}{2a}z\right)$	1, 3, 5, ...

The new Hamiltonian has been studied for the case of a fast electron. Here, the quantity of interest is the probability of exchanging a given energy $\hbar\omega$, in the phonon energy range, when the electron travels through the slab. The results of the classical theory of the energy-loss spectrum are recovered as involving the loss of one single-phonon energy. Excitation of the surface phonons proves to be the most efficient process for thicknesses up to a few thousand Å units. Many-phonon excitations occur beyond the threshold $2\hbar\omega_T$ where ω_T is the TO phonon frequency, but they have a completely negligible effect on the energy-loss spectrum.

The gain spectrum is derived for the first time. As it requires an initial thermal excitation of the phonon field, it turns out to be strongly temperature dependent and vanishes at zero temperature. This is in agreement with the observations in LiF.[1]

The over-all exchange spectrum obtained in the present theory exhibits the main features of the experimental spectrum in LiF. To obtain a quantitative agreement, however, requires the inclusion of anharmonic damping of the phonon field as has been discussed in the classical theory.[9,10]

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APPENDIX A

In Table I are listed the eigenvalues-eigenvectors of the integral equation (20) of Sec. II. The relation between λ_i and the frequency of the mode is [see Eq. (2.8)

$$\omega_i^2 = (1/4\pi)\omega_p^2\lambda_i. \tag{A1}$$

The normalization constants C_0 and C_m are given by

$$C_0 = (ka/\sinh 2ka)^{1/2} \quad 1/\sqrt{a}\,, \tag{A2}$$

$$C_m = (k^2a^2 + \tfrac{1}{4}m^2\pi^2)^{-1/2} \quad 1/\sqrt{a}\,, \tag{A3}$$

and they are chosen so that Eq. (2.28) is satisfied. The closure relation (2.29) can be verified by expanding the hyperbolic functions of the surface-mode components in Fourier series of z in the interval $[-a, +a]$.

TABLE II. Coupling functions F_i $(z_e = vt)$ of the electron to the phonon modes of the slab as functions of z_e and their Fourier transforms $J_i(\omega)$.

Eigenmodes λ	Coupling functions F_i $z_e < -a$	$-a < z_e < +a$	$z_e > +a$	Integrals J_i
λ_{0-}	e^{kz_e}	$\frac{e^{-ka}}{\cosh ka}\cosh kz_e$	e^{-kz_e}	$\frac{2k}{k^2+\omega^2/v^2}\,\frac{\cos(\omega a/v)}{v\cosh ka}$
λ_{0+}	$-e^{kz_e}$	$\frac{e^{-ka}}{\sinh ka}\sinh kz_e$	$+e^{-kz_e}$	$\frac{2k}{k^2+\omega^2/v^2}\,\frac{i\sin(\omega a/v)}{v\sinh ka}$
λ^L_m $(m=1,3,5,\ldots)$	0	$\cos\frac{m\pi}{2a}z_e$	0	$(-1)^{(m-1)/2}\,\frac{m\pi/a}{\omega^2/v^2 - m^2\pi^2/4a^2}\,\frac{\cos(\omega a/v)}{v}$
λ^L_m $(m=2,4,6,\ldots)$	0	$\sin\frac{m\pi}{2a}z_e$	0	$-(-1)^{m/2}\,\frac{im\pi/a}{\omega^2/v^2 - m^2\pi^2/4a^2}\,\frac{\sin(\omega a/v)}{v}$
λ^T_m (all $m>0$)	0	0	0	0

If the slab is made of point ions, the dispersion relation of the surface phonon modes is given by (see Ref. 12)

$$\omega_{0\pm}^2 = \omega_T^2 [1 + (\omega_p^2/2\omega_T^2)(1 \pm e^{-2ka})]. \quad \text{(A4)}$$

If the electronic polarizabilities of the ions are taken into account, then (see Refs. 12 and 7)

$$\omega_{0\pm}^2 = \omega_T^2 \cdot \frac{\epsilon_0 - 1 \pm (\epsilon_0 + 1)e^{2ka}}{\epsilon_\infty - 1 \pm (\epsilon_\infty + 1)e^{2ka}} \quad , \quad \text{(A5)}$$

which reduces to (A4) when $\epsilon_\infty = 1$ and

$$\epsilon_0 = 1 + \omega_p^2/\omega_T^2.$$

The eigenvectors are the same for both cases.

APPENDIX B

In Table II are given the coupling functions $\Gamma_i(k, z_e)$ defined in Eq. (3.5) and the corresponding integrals I_i of Eq. (5.7). The table gives the functions F_i and J_i, such that

$$\Gamma_{0\pm} = (g_0/C_0) F_{0\pm}(z_e), \; I_{0\pm} = (g_0/C_0) J_{0\pm}, \quad \text{(B1)}$$

$$\Gamma_{m\pm} = 2a g_m C_m F_{m\pm}(z_e), \; I_{m\pm} = 2a g_m C_m J_{m\pm} \quad (m \neq 0). \quad \text{(B2)}$$

The coupling constants g_i are defined by

$$g_i = (\hbar \omega_p^2 e^2 / 8\pi A \omega_i)^{1/2}. \quad \text{(B3)}$$

The normalization constants C_i are given in Appendix A, Eqs. (A2) and (A3).

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