PHYSICAL REVIEW B VOLUME 15, NUMBER 4 15 FEBRUARY 1977

Electron-phonon interaction in a dielectric slab: Effect of the electronic polarizability*

James J. Licari† and Roger Evrard
ESIS, Institut de Physique, Université de Liège, Sart Tilman, 4000 Liège 1, Belgium

(Received 21 June 1976)

The operators describing the interaction between an electron and the phonon modes of an ionic crystal slab (the bulklike sinusoidal modes and the localized surface modes) are calculated with the proper inclusion of the electronic polarizability. Since the effect of the electronic polarizability on the interaction operators exhibits itself through the amplitudes of the polarization eigenvectors, we must first derive the eigenvectors, eigenfrequencies, and amplitudes of the various phonon modes. We show that the electron–LO-phonon operator derived here is equivalent, for a very thick slab, to the Fröhlich operator for bulk LO phonons, and that the electron–surface-phonon interaction operator leads to the classical image-charge theory result for the interaction energy of an electron external to a semi-infinite crystal and the polarization eigenmodes of the crystal.

I. INTRODUCTION

In recent years, considerable theoretical effort has been directed towards a study of the modes (phonon, plasmon, etc.) existing at a free surface or at an interface. Equally interesting, and especially important from a technological point of view, is the interaction of a charged particle with these various modes. For example, the effect of the surface modes on an electron or ion approaching a free surface is important in various surface spectroscopies and adsorption studies, while the understanding of the interaction of a conduction electron with the surface modes is crucial to the study of semiconductor devices.

In this paper we are interested in the problem of a conduction electron interacting with the optical-phonon modes of an ionic semiconductor slab, that is, with both the sinusoidal bulklike modes and the surface modes.[1] These interaction operators have already been derived both for the slab[2,3] and the semi-infinite crystal.[4] However, these derivations either have assumed the ions to be nonpolarizable, that is, the high-frequency dielectric constant ϵ_∞ is taken to be unity, or they have included the electronic polarizability incorrectly. In fact, this electronic polarizability plays an important role in the interaction operators and can give a large contribution to their magnitudes. For example, the strength of the interaction with the bulklike sinusoidal modes is proportional to $(1/\epsilon_\infty - 1/\epsilon_0)^{1/2}$, where ϵ_0 is the low-frequency or static dielectric constant. For typical II-VI semiconductors and alkali halides, the effect of setting $\epsilon_\infty = 1$ is to overestimate the strength of the interaction by a factor of from 4 in the former compounds to 1.5 in the latter ones. This is certainly a non-negligible effect, especially for the technologically important II-VI compounds. For the interaction with the surface modes, the wave-vector dependence as well as the strength of the interaction is altered. This led us to rederive the interaction operators, properly treating the effect of the electronic polarizability. This derivation is the main subject of the present paper.

However, it is necessary to point out that we are not considering that part of the electronic polarization produced by the electron itself as it moves through the crystal. When we consider a bulk crystal (that is, one without surfaces), this polarization will follow the electron's motion rigidly, if it is not moving extremely fast, and will not undergo any transitions due to interaction with the electron since the characteristic frequency of the oscillations of the electronic shell ω_e is of the order of 10^{16} sec^{-1}. The electron's energy is thus lowered by a constant and is usually ignored. But as an electron approaches a surface, the pattern of electronic polarization must alter. Then the lowering of the electron's energy is not constant as it approaches the surface and should be taken into account. A measure of the extent of the polarization around the electron is $(\hbar/2m\omega)^{1/2}$, where m is the electronic mass and ω is the frequency of the polarization mode excited. For optical phonons this distance is of the order of 100 Å, while for the electronic polarization it is about 4 or 5 Å, or roughly comparable to the lattice spacing. So for the optical modes it is valid to use the continuum approximation, where the discreteness of the lattice is ignored, whereas for the electronic polarization the continuum approximation is not valid. Since this paper is based on the continuum approximation we will not be able to include the effect of this part of the electronic polarization.

For the sake of completeness, and to have the entire problem treated consistently in a single publication, we will first derive the polarization eigenvectors and eigenfrequencies. Previously, only the result of the effect of the electronic polarizability on the eigenfrequencies[1,5] has appeared in the literature (the form of the eigenvectors is unchanged) without any details of the method used or of the effect on the amplitudes of the eigenvectors.

The plan of the paper is as follows: in Sec. II we explain the notation used throughout the paper and introduce the geometry of the problem; in Sec. III we analyze the types and properties of the oscillation modes for the slab geometry based on the macroscopic electrostatic approach (this facilitates comparison with and understanding of the modes subsequently obtained via a microscopic approach); in Sec. IV we begin the microscopic approach and find the normal modes by evaluating the local electric field at an ion site; in Sec. V we consider the free-polarization Hamiltonian and give physical arguments for its form; in Sec. VI the electron-phonon interaction operator is derived showing the proper dependence on the electronic polarizability; in Sec. VII we consider an electron outside the slab interacting with the polarization eigenmodes and compare this interaction energy with that gotten from classical electrostatics; and in Sec. VIII we give a brief summary of our results. Finally, in the Appendix we show that in the limit when the slab thickness becomes large, the interaction Hamiltonian for an electron and the sinusoidal bulklike modes present in the slab is equivalent to the usual Fröhlich Hamiltonian for an electron interacting with bulk longitudinal-optical phonons.

II. NOTATION AND GEOMETRY OF THE PROBLEM

Since the primary purpose of this paper is to derive the correct form of the electron-phonon interaction operator, we will, for the most part, use the notation of Lucas, Kartheuser, and Badro[2] (hereafter LKB) who have previously derived this interaction term without the inclusion of the electronic polarizability. The Einstein summation convention, where repeated indices indicates a sum over the values taken by those indices, is used throughout.

Because we are considering a semiconductor slab, the geometry is that of Fig. 1 which is nearly identical to the corresponding figure of Ref. 1. The slab lies between $\pm a$ with faces normal to the z axis and extends to infinity in the x and y directions. The other indications on the figure will be explained in the following sections as they become relevant.

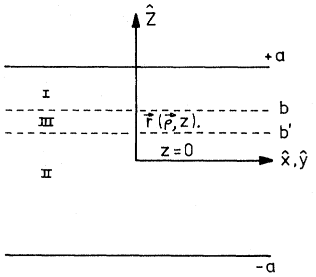

FIG. 1. Geometry relevant to the discussion of the dielectric slab.

III. MACROSCOPIC ANALYSIS

The understanding of the physical meaning of the different vibrational modes that will be obtained later on by a microscopic approach is greatly facilitated if one first considers the problem using the classical macroscopic approach. Therefore, in this section we consider the crystal slab from the point of view of classical electrostatics, that is, based on the equations

$$\vec{\nabla}\cdot\vec{D}=4\pi\rho_0(\vec{r})\,, \tag{3.1a}$$

$$\vec{D}(\vec{r})=\epsilon\vec{E}(\vec{r}) \tag{3.1b}$$

$$=\vec{E}(\vec{r})+4\pi\vec{P}(\vec{r})\,, \tag{3.1c}$$

and

$$\vec{E}(\vec{r})=-\vec{\nabla}\phi(\vec{r})\,, \tag{3.1d}$$

where $\vec{E}(\vec{r})$, $\vec{D}(\vec{r})$, $\vec{P}(\vec{r})$, and $\phi(\vec{r})$ are the electric field, electric displacement, electric polarization, or dipole moment per unit volume, and scalar potential; $\rho_0(\vec{r})$ is the free charge density; and ϵ is the dielectric constant of the slab. Since the system is translationally invariant along the surface, one may take $\phi(\vec{r})$ of the form

$$\phi(\vec{r})=\phi(z)\,e^{i\vec{k}\cdot\vec{\rho}}\,, \tag{3.2}$$

where $\vec{\rho}$ and $\vec{k}$ are two-dimensional position and wave vectors in the plane of the surface. If we consider the case where $\rho_0(\vec{r})=0$ (free oscillations) the above equations lead to

$$\epsilon\left(\frac{\partial^2}{\partial z^2}-k^2\right)\phi(z)=0\,. \tag{3.3}$$

Besides the trivial solution $\phi(z)=0$, there are two possible solutions to this equation, either $\epsilon=0$ or the quantity in large parentheses is zero.

Consider first the case where $\epsilon=0$ inside the slab. If we write the frequency-dependent dielectric constant for a semiconductor in the usual way, that is,

$$\epsilon(\omega)=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/(1-\omega^2/\omega_{\mathrm{TO}}^2)\,, \tag{3.4}$$

where ω_{TO} is the restrahlen or transverse-optical (TO) frequency, then for $\epsilon = 0$ the frequency is $\omega^2 = \omega_{\mathrm{TO}}^2(\epsilon_0/\epsilon_\infty)$, which is the longitudinal-optical (LO) phonon frequency according to the Lyddane-Sachs-Teller relation. In this case, the solution of Eq. (3.3) is an arbitrary function of z which we will write

$$\phi(z) = \sum_k (\phi_a \sin k_z z + \phi_b \cos k_z z) . \tag{3.5}$$

The solutions of Eq. (3.3) in the regions outside the slab ($|z| > a$) where $\epsilon = 1$ are of the form $\phi(z) = \phi_\pm e^{\pm kz}$, where the plus sign is chosen for $z < -a$ and the minus sign for $z > +a$ in order that $\phi(z)$ remain finite at $z = \pm\infty$. The amplitudes ϕ_a, ϕ_b, ϕ_+, and ϕ_- are determined by the boundary conditions on $\vec{\mathrm{E}}$ and $\vec{\mathrm{D}}$ at the two surfaces. These conditions yield $\phi_\pm = 0$ so that $\phi(z)$, $\vec{\mathrm{E}}(\vec{\mathrm{r}})$, and $\vec{\mathrm{D}}(\vec{\mathrm{r}})$ are zero outside the slab for this mode. Inside the slab the matching of boundary conditions is satisfied in two ways, either $\phi_a = 0$ or $\phi_b = 0$. Thus we have two solutions with polarization vectors

$$\vec{\mathrm{P}}_+^m(\vec{\mathrm{r}}) = \frac{\phi_b}{4\pi a} e^{i\vec{\mathrm{k}}\cdot\vec{\rho}} \left(i\vec{\mathrm{k}} a \cos\frac{m\pi}{2a} z - \hat{z}\,\frac{m\pi}{2} \sin\frac{m\pi}{2a} z \right)$$

$$(m = 1, 3, \ldots) \tag{3.6a}$$

and

$$\vec{\mathrm{P}}_-^m(\vec{\mathrm{r}}) = \frac{\phi_a}{4\pi a} e^{i\vec{\mathrm{k}}\cdot\vec{\rho}} \left(i\vec{\mathrm{k}} a \sin\frac{m\pi}{2a} z + \hat{z}\,\frac{m\pi}{2} \cos\frac{m\pi}{2a} z \right)$$

$$(m = 2, 4, \ldots) , \tag{3.6b}$$

where $\hat{z}$ is the unit vector in the z direction. We have chosen to give the polarization vectors here for comparison with the results of the microscopic calculation in Sec. IV. Because the slab possesses a plane of mirror symmetry at $z = 0$, the polarization vectors exhibit even or odd symmetry with respect to this plane, this being indicated by the $\pm$ subscripts. Figure 2 shows the components of $\vec{\mathrm{P}}_\pm^m(\vec{\mathrm{r}})$ for $m = 1$ and 2.

In the case where $\epsilon \neq 0$ inside the slab, $\phi(z)$ is a linear combination of exponentials, that is,

$$\phi(z) = \phi_a e^{kz} + \phi_b e^{-kz} . \tag{3.7}$$

Outside the slab, $\phi(z)$ is again equal to $\phi_\pm e^{\pm kz}$. Matching boundary conditions there gives for this mode the polarization fields

$$\vec{\mathrm{P}}_+^0(\vec{\mathrm{r}}) = -\phi_a k \,\frac{1-\epsilon}{4\pi} e^{i\vec{\mathrm{k}}\cdot\vec{\rho}}$$

$$\times (i\hat{k} \cosh kz + \hat{z} \sinh kz) \tag{3.8a}$$

and

$$\vec{\mathrm{P}}_-^0(\vec{\mathrm{r}}) = -\phi_a k \,\frac{1-\epsilon}{4\pi} e^{i\vec{\mathrm{k}}\cdot\vec{\rho}}$$

$$\times (i\hat{k} \sinh kz + \hat{z} \cosh kz) , \tag{3.8b}$$

where $\hat{k}$ is the unit two-dimensional wave vector. These two polarization vectors describe the surface-optical (SO) modes associated with the slab. The components of $\vec{\mathrm{P}}_\pm^0(\vec{\mathrm{r}})$ are also shown in Fig. 2, where we see that the polarization decreases exponentially on moving away from the surfaces. Their frequencies are given by

$$(1+\epsilon)/(1-\epsilon) = \pm e^{-2ka} , \tag{3.9}$$

gotten from the boundary conditions, so that using $\epsilon(\omega)$ of Eq. (3.4), we find

$$\omega_\pm^2 = \omega_{\mathrm{TO}}^2 \,\frac{(\epsilon_0 + 1) \mp (\epsilon_0 - 1)\, e^{-2ka}}{(\epsilon_\infty + 1) \mp (\epsilon_\infty - 1)\, e^{-2ka}} . \tag{3.10}$$

The + (−) sign on $\omega_\pm^2$ indicates the even (odd) mode frequency and is to be associated with the upper (lower) sign on the right-hand side of Eq. (3.10).

The above macroscopic electrostatic approach was able to give us the LO and SO modes because for both of these modes there exists a polarization charge density. For the LO modes there is both a volume density $\rho' = -\vec{\nabla}\cdot\vec{\mathrm{P}}$ and a surface density $\sigma' = -\vec{\mathrm{P}}\cdot\hat{n}$ ($\hat{n}$ is the unit normal to the surface

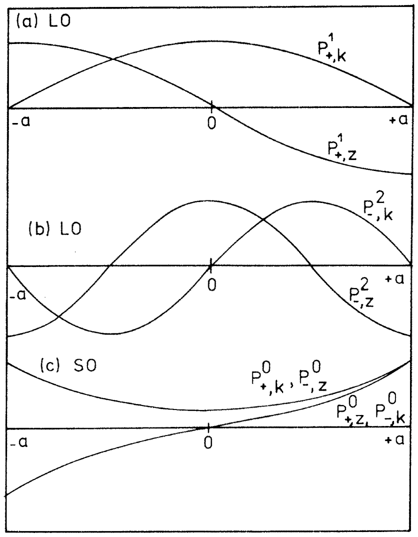

FIG. 2. z dependence of the $\hat{k}$ and $\hat{z}$ components of (a) the even LO mode $\vec{\mathrm{P}}_+^1(\vec{\mathrm{r}})$ of Eq. (3.6a), (b) the odd LO mode $\vec{\mathrm{P}}_-^2(\vec{\mathrm{r}})$ of Eq. (3.6b), and (c) the even and odd SO modes $\vec{\mathrm{P}}_\pm^0(\vec{\mathrm{r}})$ of Eqs. (3.8a) and (3.8b). Note that for the LO modes the $\hat{k}$ components vanish at $\pm a$ in accordance with the boundary condition on $\vec{\mathrm{E}}$. For both the LO and SO modes, the finite $\hat{z}$ components at $\pm a$ result in a surface charge density. The relative amplitudes of the $\hat{k}$ and $\hat{z}$ components have not been portrayed in the figure.

pointing into the vacuum), while for the SO modes there is a surface density alone. It is this polarization charge which acts as a source for the fields associated with these modes. Since $\vec{\nabla}\cdot\vec{P}=0$ (also $\vec{P}\circ\hat{n}=0$ at the surface) for a transverse mode, we cannot expect to find transverse bulk modes via the macroscopic approach. We should point out that the results of this section include the effects of the electronic polarizability since $\epsilon_\infty \neq 1$, and they are identical to those of LKB and those of Sec. IV.

In Sec. IV we begin a microscopic approach, microscopic in that we consider the forces acting on an individual ion and formulate the problem in terms of relative ionic displacements and the local electric field (rather than the macroscopic field $\vec{E}$). The electronic polarization will be introduced here via the polarizability α. This approach will give us, besides the LO and SO modes found above, the TO modes associated with the slab; these modes are also needed to formulate the Hamiltonian. In constructing the electron-phonon interaction operator, besides the functional form of the polarization eigenvectors which we found in this section for the LO and SO modes, we also need the polarization amplitudes. These amplitudes are gotten from the orthonormality and completeness conditions imposed on the eigenvectors, which can only be formulated in the microscopic framework.

IV. EQUATION OF MOTION AND NORMAL MODES

As mentioned previously, the basic approach used in this section is that of LKB, modified to include the electronic polarizability of the ions.

We consider an ionic crystal consisting of one pair of positive and negative ions per unit cell, the magnitude of the charge on each being e. Since we are interested in the long-wavelength optical modes, we will use the continuum model where we write the displacement of the positive and negative ions as $\vec{u}_+(\vec{r},t)$ and $\vec{u}_-(\vec{r},t)$, respectively, $\vec{r}$ being the position vector of the center of the cell containing the pair of ions. The equation of motion for the relative displacement of the positive and negative ions

$$\vec{u}(\vec{r},t)=\vec{u}_+(\vec{r},t)-\vec{u}_-(\vec{r},t)\,, \tag{4.1}$$

is

$$\mu\frac{d^2\vec{u}}{dt^2}(\vec{r},t)=-\mu\omega_0^2\vec{u}(\vec{r},t)+e\vec{E}^l(\vec{r},t)\,, \tag{4.2}$$

where $\mu=M_+M_-/(M_++M_-)$ is the reduced mass of the ion pair or reduced mass per unit cell, ω_0 is the frequency associated with the short-range force between ions, and $\vec{E}^l(\vec{r},t)$ is the local field at the position of the ions. The oscillating ions produce a polarization field $\vec{P}(\vec{r},t)$ consisting of two parts: the ionic polarization produced by the relative separation of the positive and negative ions when the crystal vibrates in an optical mode, and the electronic polarization caused by the electric field associated with the optical mode. So we write $\vec{P}(\vec{r},t)$ as

$$\vec{P}(\vec{r},t)=ne\vec{u}(\vec{r},t)+n\alpha\vec{E}^l(\vec{r},t)\,, \tag{4.3}$$

where n is the number of ion pairs (or unit cells) per unit volume, and α is the electronic polarizability per ion pair.

Following the method of Fuchs and Kliewer and LKB for calculating the local field $\vec{E}^l(\vec{r},t)$ at the position $\vec{r}=(\vec{\rho},z)$, we divide the crystal into three slabs whose faces lie parallel to the external surfaces of the crystal, as in Fig. 1. Regions I and II are sufficiently far from $\vec{r}$ that the distribution of polarization in these regions can be taken to be continuous and the field produced at $\vec{r}$ can be calculated macroscopically. The contribution to the field at $\vec{r}$ of a unit volume of polarization charge located at $\vec{r}'$ in one of these two regions is[6]

$$\begin{aligned}E_i(\vec{r},\vec{r}';t)&=\frac{3\hat{r}_i\hat{r}_j-\delta_{ij}}{|\vec{r}-\vec{r}'|^3}P_j(\vec{r}',t)\\&=T_{ij}(\vec{r}-\vec{r}')P_j(\vec{r}',t)\,,\end{aligned} \tag{4.4}$$

where i and j indicate Cartesian components, and $\hat{r}$ is a unit vector. Therefore, the total contribution of regions I and II to the local field at $\vec{r}$, which we will call $\vec{E}^a(\vec{r},t)$, is

$$E_i^a(\vec{r},t)=\int_{\mathrm{I,\,II}}T_{ij}(\vec{r}-\vec{r}')P_j(\vec{r}',t)\,d\vec{r}'\,. \tag{4.5}$$

As indicated, the integral is in principle only over the regions I and II. However, we are interested only in modes with large wavelengths, that is, far larger than the dimensions of the unit cell. Indeed, in the framework of Fröhlich's polaron theory[7] it is assumed that these are the only modes to have an appreciable interaction with conduction band electrons or valence band holes. The thickness of region III can then be taken large compared to the dimensions of the unit cell (so that regions I and II can be treated macroscopically) but small compared to the phonon wavelength. Therefore, the integral in Eq. (4.5) can be extended to the entire crystal slab without introducing any appreciable error.

Based on these assumptions, we use the well-known result of Lorentz[8] to describe the contribution of region III to the local field. This field can be written for the slab geometry as

$$E_i^b(\vec{r},t)=\eta_{ij}P_j(\vec{r},t)\,, \tag{4.6}$$

where

$$\eta_{ij} = \begin{pmatrix} \frac{4}{3}\pi & 0 & 0 \\ 0 & \frac{4}{3}\pi & 0 \\ 0 & 0 & -\frac{8}{3}\pi \end{pmatrix}. \tag{4.7}$$

Then the total local field at $\vec{r}$ is the sum of $\vec{E}^a$ and $\vec{E}^b$, so that its ith component is

$$E_i^l(\vec{r}, t) = \eta_{ij} P_j(\vec{r}, t) + \int_{\text{slab}} T_{ij}(\vec{r} - \vec{r}\,') P_j(\vec{r}\,', t)\, d\vec{r}\,'. \tag{4.8}$$

We continue now with the method of LKB to arrive at the equation giving the normal modes of the system. Differentiating Eq. (4.3) twice with respect to time and using Eq. (4.2), with the local electric field given above, one finds

$$\begin{aligned} \ddot{P}_i(\vec{r}, t) = -\omega_0^2 P_i(\vec{r}, t) &+ \sigma \eta_{ij} P_j(\vec{r}, t) \\ &+ \sigma \int T_{ij}(\vec{r} - \vec{r}\,') P_j(\vec{r}\,', t)\, d\vec{r}\,' \\ &+ n\alpha\eta_{ij} \ddot{P}_j(\vec{r}, t) \\ &+ n\alpha \int T_{ij}(\vec{r} - \vec{r}\,') \ddot{P}_j(\vec{r}\,', t)\, d\vec{r}\,', \end{aligned} \tag{4.9}$$

where

$$\sigma = n\alpha\omega_0^2 + ne^2/\mu. \tag{4.10}$$

Assuming that the polarization field has a sinusoidal time dependence, that is, $\vec{P}(\vec{r}, t) = \vec{P}(\vec{r}) e^{i\omega t}$, where ω is a normal frequency of vibration, and defining

$$\lambda_0 = 4\pi\omega_0^2/\omega_p^2, \quad \lambda = 4\pi\omega^2/\omega_p^2, \tag{4.11}$$

$$\gamma_{ij} = \frac{(\lambda - \lambda_0)(\delta_{ij} - n\alpha\eta_{ij})}{1 - n\alpha(\lambda - \lambda_0)}, \tag{4.12}$$

and

$$\Gamma_{ij} = -\eta_{ij}/[1 - n\alpha(\lambda - \lambda_0)], \tag{4.13}$$

we arrive at

$$(\gamma_{ij} - \Gamma_{ij}) P_j(\vec{r}) = -\int T_{ij}(\vec{r} - \vec{r}\,') P_j(\vec{r}\,', t)\, d\vec{r}\,'. \tag{4.14}$$

In Eq. (4.11), ω_p is the ion plasma frequency defined by $\omega_p^2 = 4\pi ne^2/\mu$.

To write the integral on the right-hand side of Eq. (4.14) in a more transparent form, one can introduce the two-dimensional Fourier transform of $\vec{P}(\vec{r})$,

$$\vec{P}(\vec{r}) = \frac{A}{4\pi^2} \int d\vec{k}\, e^{i\vec{k}\cdot\vec{\rho}}\, \vec{P}(\vec{k}, z), \tag{4.15}$$

where A is the area of the slab surface (the factor A will drop out of all physical results). Similarly, the Fourier transform of $T_{ij}(\vec{r} - \vec{r}\,')$ is written

$$T_{ij}(\vec{r} - \vec{r}\,') = -\int d\vec{k}\, \frac{K_i K_j}{2\pi k} e^{i\vec{k}\cdot(\vec{\rho} - \vec{\rho}\,')} e^{-k|z - z'|}, \tag{4.16}$$

with the three-dimensional vector $\vec{K}$ defined as $\vec{K} = (\vec{k}, ik\theta(z - z'))$. As is usual, the Θ function is given by

$$\Theta(z - z') = \begin{cases} +1, & z > z', \\ -1, & z < z'. \end{cases} \tag{4.17}$$

Using the Fourier transforms defined above, Eq. (4.14) takes the form

$$(\gamma_{ij} - \Gamma_{ij}) P_j(\vec{k}, z) = \frac{2\pi}{k} \int dz' K_i K_j \times e^{-k|z - z'|} P_j(\vec{k}, z'). \tag{4.18}$$

With the indices i and j denoting the three Cartesian components of the vectors concerned, let us choose the x axis to lie along $\vec{k}$. Since the z axis is defined as normal to the surface, this makes the y axis lie also in the surface plane and be normal to $\vec{k}$. From this point on we will indicate the coordinate directions by $\hat{k}$, $\hat{y}$, and $\hat{z}$. In this system then, the vector $\vec{K}$ has only $\hat{k}$ and $\hat{z}$ components, as indicated in its definition.

We now consider Eq. (4.18) for each of the coordinate directions. When we take the $\hat{y}$ component of this equation we find

$$(\gamma_y - \Gamma_y) P_y(\vec{k}, z) = 0, \tag{4.19}$$

since $\vec{K}$ has no $\hat{y}$ component and both γ_{ij} and Γ_{ij} are diagonal. Then for $P_y(\vec{k}, z) \neq 0$ we must have $\gamma_y = \Gamma_y$, and so the frequency of this mode is given by

$$\omega_{\text{TO}}^2 = \omega_0^2 - \frac{\frac{1}{3}\omega_p^2}{1 - \frac{4}{3}\pi n\alpha}. \tag{4.20}$$

This is the TO frequency associated with the infrared resonance of the ionic crystal. This is a purely transverse mode since the polarization is normal to the surface wave vector $\vec{k}$. Since the polarization can be an arbitrary function of z, we may expand it in a complete set of orthonormal eigenfunctions. Following LKB we choose the eigenfunctions in Table I, indicated by $P_{y,\pm}^j(z)$. From Eq. (4.18) it is seen that this TO mode is completely uncoupled to the remaining modes of the system. Thus the eigenfunctions of the $P_{y,p}^j(z)$ also satisfy a closure relation of the form

$$\sum_{j,p} P_{y,p}^j(z) P_{y,p}^{*j}(z') = \delta(z - z'), \tag{4.21}$$

where p is the parity index taking the values + and −.

TABLE I. Polarization eigenvectors for the dielectric slab.

Mode	Frequency	Eigenvectors	
TO	ω_{TO}	$P^{j}_{y,+}(z)=ia^{-1/2}\cos(j\pi z/a)$	$j=1,2,\ldots$
		$P^{j}_{y,-}(z)=ia^{-1/2}\sin(j\pi z/a)$	
SO	ω_{0+}	$\vec{\pi}^{0}_{+}(\vec{\mathrm{k}},z)=C_0(i\cosh kz,\ \sinh kz)$	
	ω_{0-}	$\vec{\pi}^{0}_{-}(\vec{\mathrm{k}},z)=C_0(i\sinh kz,\ \cosh kz)$	
LO	ω_{LO}	$\vec{\pi}^{m}_{+}(\vec{\mathrm{k}},z)=C_m\left(ika\cos\frac{m\pi}{2a}z,-\frac{m\pi}{2}\sin\frac{m\pi}{2a}z\right)$	$m=1,3,\ldots$
		$\vec{\pi}^{m}_{-}(\vec{\mathrm{k}},z)=C_m\left(ika\sin\frac{m\pi}{2a}z,\ \frac{m\pi}{2}\cos\frac{m\pi}{2a}z\right)$	$m=2,4,\ldots$
TO	ω_{TO}	$\vec{\pi}^{m}_{+}(\vec{\mathrm{k}},z)=C_m\left(\frac{im\pi}{2}\cos\frac{m\pi}{2a}z,ka\sin\frac{m\pi}{2a}z\right)$	$m=2,4,\ldots$
		$\vec{\pi}^{m}_{-}(\vec{\mathrm{k}},z)=C_m\left(-\frac{im\pi}{2}\sin\frac{m\pi}{2a}z,ka\cos\frac{m\pi}{2a}z\right)$	$m=1,3,\ldots$

To find the other modes, we write the $\hat{k}$ and $\hat{z}$ components of Eq. (4.18), again using the fact that γ_{ij} and Γ_{ij} are diagonal. These are

$$\left(\frac{(\lambda-\lambda_0)(1-\frac{4}{3}\pi n\alpha)+\frac{4}{3}\pi}{1-n\alpha(\lambda-\lambda_0)}\right)P_k(\vec{\mathrm{k}},z)=2\pi k\int_{-a}^{+a}dz'\,e^{-k|z-z'|}[P_k(\vec{\mathrm{k}},z')+i\Theta(z-z')P_z(\vec{\mathrm{k}},z')] \tag{4.22a}$$

and

$$\left(\frac{(\lambda-\lambda_0)(1+\frac{8}{3}\pi n\alpha)-\frac{8}{3}\pi}{1-n\alpha(\lambda-\lambda_0)}\right)P_z(\vec{\mathrm{k}},z)=2\pi k\int_{-a}^{+a}dz'\,e^{-k|z-z'|}[i\Theta(z-z')P_k(\vec{\mathrm{k}},z')-P_z(\vec{\mathrm{k}},z')]\,. \tag{4.22b}$$

Although the left-hand sides differ by the inclusion of the α dependence, Eqs. (4.22a) and (4.22b) are otherwise identical to the coupled equations derived and solved by Fuchs and Kliewer in their treatment of the normal modes of an ionic crystal slab. We therefore find solutions having the same form. There are three types of modes: modes whose frequency is the bulk transverse-optical frequency, the TO modes; modes whose frequency is the bulk longitudinal-optical frequency, the LO modes; and modes whose amplitudes decrease exponentially on moving away from the surfaces, the surface-optical or SO modes. The frequencies of these modes are as follows:

$$\omega^2_{\mathrm{TO}}=\omega_0^2-\tfrac{1}{3}\,\omega_p^2/(1-\tfrac{4}{3}\pi n\alpha)\,, \tag{4.20}$$

$$\omega^2_{\mathrm{LO}}=\omega_0^2+\tfrac{2}{3}\,\omega_p^2/(1+\tfrac{8}{3}\pi n\alpha)\,, \tag{4.23a}$$

and

$$\omega^2_{0\pm}=\omega_0^2+\frac{\omega_p^2}{2}\,\frac{\frac{1}{3}\mp e^{-2ka}}{1+2\pi n\alpha(\frac{1}{3}\mp e^{-2ka})}\,. \tag{4.23b}$$

(Fuchs and Kliewer[1] indicated that the inclusion of the electronic polarizability would result in the above frequencies.) Again for the SO modes, ω_{0+} (ω_{0-}) must be associated with the upper (lower) sign on the right-hand side of Eq. (4.23b), which is equivalent to Eq. (3.10). The eigenvectors for all the modes are given in Table I, indicated by $\vec{\pi}^{m}_{p}(\vec{\mathrm{k}},z)$; they are the eigenvectors of LKB. The normalization constants of LKB are

$$C_0=(k/\sinh 2ka)^{1/2} \tag{4.24a}$$

and

$$C_m=\frac{1/\sqrt{a}}{(k^2a^2+\frac{1}{4}m^2\pi^2)^{1/2}}\,. \tag{4.24b}$$

The vectors $\vec{\pi}^{m}_{p}(\vec{\mathrm{k}},z)$ are two-dimensional normalized eigenvectors with $\hat{k}$ and $\hat{z}$ components alone, and the connection between them and $\vec{\mathrm{P}}(\vec{\mathrm{k}},z)$ is

$$\vec{\pi}(\vec{\mathrm{k}},z)=1/\beta\,[P_k(\vec{\mathrm{k}},z),P_z(\vec{\mathrm{k}},z)]\,,$$

where β is taken to be $e(n/A)^{1/2}$ in order that $\vec{\mathrm{P}}(\vec{\mathrm{k}},z)$ have the proper units. $\vec{\pi}^{m}_{p}(\vec{\mathrm{k}},z)$ as defined satisfy the orthonormality relation

$$\int_{-a}^{+a}dz\,\vec{\pi}^{*m}_{p}(\vec{\mathrm{k}},z)\cdot\vec{\pi}^{m'}_{p'}(\vec{\mathrm{k}},z)=\delta_{mm'}\,\delta_{pp'}\,, \tag{4.25}$$

and the closure relation

$$\sum_{m,p} \pi^{*\,m}_{p,i}(\vec{k},z)\,\pi^{m}_{p,j}(\vec{k},z') = \delta_{ij}\,\delta(z-z') . \qquad (4.26)$$

Both these relations will be used in deriving the Hamiltonian. In Eqs. (4.25) and (4.26), only the modes whose polarization is confined to the plane defined by the $\hat{k}$ and $\hat{z}$ vectors are to be included, that is, the $\vec{\pi}^{m}_{p}(\vec{k},z)$. As pointed out earlier, the $P^{j}_{y,p}(z)$ are completely uncoupled to the other modes and satisfy their own closure and orthonormality relations.

We have found in this section all the modes obtained by the macroscopic method of Sec. III, that is, the LO and SO modes. As explained there, the TO modes found in this section could not be gotten by the macroscopic method because they do not produce a polarization charge density.

As regards the p-labeling of the modes, our notation differs somewhat from LKB. For the LO and TO modes, the index m denotes the $\hat{z}$ component of the wave vector through $k_z = m\pi/2a$. The surface modes are indicated by $m=0$.

V. FREE-POLARIZATION HAMILTONIAN

In deriving the Hamiltonian, we will need the explicit relationship between the two-dimensional Fourier transform of $\vec{P}(\vec{r})$ and that of $\vec{E}(\vec{r})$ and $\vec{u}(\vec{r})$. We proceed as follows.

Using Eq. (4.8) and Fourier transforming the vectors $\vec{E}(\vec{r})$ and $\vec{P}(\vec{r})$ and the tensor $T_{ij}(\vec{r}-\vec{r}\,')$, we write for the ith component (i is either $\hat{k}$, $\hat{y}$, or $\hat{z}$) of $\vec{E}(\vec{k},z)$,

$$E_i(\vec{k},z) = \eta_{ij}\,P_j(\vec{k},z) - \frac{2\pi}{k}\int_{-a}^{+a} dz'\,K_i K_j\,e^{-k|z-z'|}P_j(\vec{k},z') . \qquad (5.1)$$

Since the true transverse polarization described by the eigenvectors $P^{j}_{y}(z)$ is completely uncoupled from the $\vec{\pi}^{m}_{p}(\vec{k},z)$ modes, and our interest lies solely with the $\vec{\pi}^{m}_{p}(\vec{k},z)$ modes, we consider only these. So we write the $\hat{k}$ and $\hat{z}$ components of Eq. (5.1):

$$E_k(\vec{k},z) = \tfrac{4}{3}\pi P_k(\vec{k},z) - 2\pi k\int_{-a}^{+a} dz'\,e^{-k|z-z'|}\left[P_k(\vec{k},z') + i\,\Theta(z-z')\,P_z(\vec{k},z')\right] \qquad (5.2a)$$

and

$$E_z(\vec{k},z) = -\tfrac{8}{3}\pi P_z(\vec{k},z) - 2\pi k\int_{-a}^{+a} dz'\,e^{-k|z-z'|}\left[i\Theta(z-z')\,P_k(\vec{k},z') - P_z(\vec{k},z')\right] . \qquad (5.2b)$$

Using the eigenvectors given in Table I, we find from the above equations that $\vec{E}(\vec{k},z)$ is related to $\vec{P}(\vec{k},z)$ by

$$\vec{E}^{m}_{p}(\vec{k},z) = \phi^{m}_{p}\,\vec{P}^{m}_{p}(\vec{k},z) , \qquad (5.3)$$

where ϕ^{m}_{p} is defined as follows: TO modes,

$$\phi^{m}_{p} = \tfrac{4}{3}\pi ; \qquad (5.4a)$$

LO modes,

$$\phi^{m}_{p} = -\tfrac{8}{3}\pi ; \qquad (5.4b)$$

SO modes,

$$\phi^{0}_{\pm} = -2\pi\left(\tfrac{1}{3} \mp e^{-2ka}\right) . \qquad (5.4c)$$

In Eq. (5.3), the fact that the vectors bear the indices m, p indicates that they are two-dimensional vectors with $\hat{k}$ and $\hat{z}$ components alone.

From the Fourier transform of Eq. (4.3) we can find the relation between $\vec{u}(\vec{k},z)$ and $\vec{P}(\vec{k},z)$. This is

$$\vec{u}^{m}_{p}(\vec{k},z) = (1/ne)\,(1 - n\alpha\phi^{m}_{p})\,\vec{P}^{m}_{p}(\vec{k},z) . \qquad (5.5)$$

We are now in a position to consider the free-polarization Hamiltonian, i.e., the Hamiltonian describing the free vibrations of the lattice in the absence of external charges. We again point out that in none of the following do we include the true transverse $P^{j}_{y}(z)$ modes since these modes, and the Hamiltonian describing them, must be treated completely independently of the $\vec{\pi}^{m}_{p}(\vec{k},z)$ modes.

The free-polarization Hamiltonian is composed of three terms and is written as follows:

$$H_F = n\,\frac{\mu}{2}\int d\vec{r}\left(\frac{d}{dt}\vec{u}(\vec{r})\right)^2 + \frac{n}{2}\mu\omega_0^2\int d\vec{r}\,\vec{u}^{2}(\vec{r}) - \frac{n}{2}\int d\vec{r}\,e\vec{E}(\vec{r})\cdot\vec{u}(\vec{r}) . \qquad (5.6)$$

The first term is the kinetic energy of the oscillating ions. At the frequencies considered here, the electron cloud around each ion follows adiabatically the ionic oscillations and so introduces no additional inertia. The second term is the potential energy associated with the short-range restoring force $-\mu\omega_0^2\vec{u}(\vec{r})$ acting between ion pairs. If the ions were uncharged their oscillation frequency would be determined by this force alone and would be ω_0. However, since the oscillating ions are charged, a long-range electric field is produced which alters the oscillation frequency. Equations (4.20) and (4.23a) show that this field stiffens the lattice in the LO mode and softens it in the TO mode. The third term in H_F accounts for this effect and is the potential energy of the ions in the dipole field $\vec{P}$.

We now Fourier transform the Hamiltonian H_F according to Eq. (4.15), but changing the integral over $\vec{k}$ to a sum by using $\int d\vec{k} \to (4\pi^2/A)\sum_{\vec{k}}$. The vectors $\vec{u}(\vec{k},z)$, $\vec{E}(\vec{k},z)$, and $\vec{P}(\vec{k},z)$ are now considered as quantum-mechanical operators and are written as linear combinations of the corresponding eigenvectors. For example, we have for the displacement $\vec{u}(\vec{k},z)$ that

$$\vec{u}(\vec{k},z)=\sum_{m,p} B_{m,p} \times [a_{m,p}(\vec{k})+a^{\dagger}_{m,p}(-\vec{k})]\,\vec{u}^{m}_{p}(\vec{k},z)\,, \qquad (5.7a)$$

and for its conjugate momentum $\vec{p}(\vec{k},z) = nA\mu[d\vec{u}^{\dagger}(\vec{k},z)/dt]$,

$$\vec{p}(\vec{k},z)=inA\mu\sum_{m,p}\omega_{m,p}B_{m,p} \times [a^{\dagger}_{m,p}(-\vec{k})-a_{m,p}(\vec{k})]\,\vec{u}^{m}_{p}(\vec{k},z)\,. \qquad (5.7b)$$

The vectors $\vec{u}(\vec{k},z)$ and $\vec{p}(\vec{k},z)$ satisfy the commutation relation

$$[p_i(\vec{k},z),u_j(\vec{k}',z')]=(\hbar/i)\,\delta_{ij}\,\delta_{\vec{k},\vec{k}'}\,\delta(z-z')\,. \qquad (5.8)$$

In the above equations, $a^{\dagger}_{m,p}(\vec{k})$ and $a_{m,p}(\vec{k})$ are creation and annihilation operators, respectively, for the m,p mode. They satisfy the usual commutation relation

$$[a_{m,p}(\vec{k}),a^{\dagger}_{m',p'}(\vec{k}')]=\delta_{m,m'}\delta_{p,p'}\delta_{\vec{k},\vec{k}'}\,. \qquad (5.9)$$

For the vectors $\vec{E}(\vec{k},z)$ and $\vec{P}(\vec{k},z)$ we write similarly

$$\vec{E}(\vec{k},z)=\sum_{m,p}B_{m,p}[a_{m,p}(\vec{k})+a^{\dagger}_{m,p}(-\vec{k})]\,\vec{E}^{m}_{p}(\vec{k},z) \qquad (5.10)$$

and

$$\vec{P}(\vec{k},z)=\sum_{m,p}B_{m,p}[a_{m,p}(\vec{k})+a^{\dagger}_{m,p}(-\vec{k})]\,\vec{P}^{m}_{p}(\vec{k},z)\,. \qquad (5.11)$$

Using Eqs. (5.3) and (5.5), the orthonormality relations for the $\vec{\pi}^{m}_{p}(\vec{k},z)$, and the above commutation relation for $a_{m,p}(\vec{k})$ and $a^{\dagger}_{m,p}(\vec{k})$, H_F becomes

$$H_F=2A\sum_{\vec{k}}\sum_{m,p}(\beta B_{m,p})^2\lambda_{m,p}(1-n\alpha\phi^{m}_{p})^2 \times[a^{\dagger}_{m,p}(\vec{k})a_{m,p}(\vec{k})+\tfrac{1}{2}]\,, \qquad (5.12)$$

where we have used the fact that $\lambda_{m,p}$ is related to ϕ^{m}_{p} by

$$\lambda_{m,p}=\lambda_0-\phi^{m}_{p}/(1-n\alpha\phi^{m}_{p})\,. \qquad (5.13)$$

Since $\vec{u}^{m}_{p}(\vec{k},z)$ as defined is dimensionless, $B_{m,p}$ must have the units of length. So we choose

$$B_{m,p}=(\hbar/2\mu\omega_{m,p})^{1/2}(1-n\alpha\phi^{m}_{p})^{-1}\,. \qquad (5.14)$$

Since $\beta=e(n/A)^{1/2}$, we have for the Hamiltonian

$$H_F=\sum_{\vec{k}}\sum_{m,p}\hbar\omega_{m,p}[a^{\dagger}_{m,p}(\vec{k})a_{m,p}(\vec{k})+\tfrac{1}{2}]\,. \qquad (5.15)$$

As throughout this section, the sum over m,p runs over the TO, LO, and SO modes as given by Table I and by Eqs. (4.20), (4.23a), and (4.23b).

$B_{m,p}$, as given above, is essentially the amplitude of the polarization field $\vec{P}(\vec{k},z)$. The electron-phonon interaction operator is proportional to $\vec{P}(\vec{k},z)$ and therefore to $B_{m,p}$. Since $B_{m,p}$ depends on α, the interaction operator derived in the next section will differ from that given by LKB.

VI. ELECTRON-PHONON INTERACTION

The interaction energy of an electron and the polarization modes just described is written[9]

$$H'=-\int\vec{D}(\vec{r}-\vec{r}')\cdot\vec{P}(\vec{r})\,d\vec{r}\,, \qquad (6.1)$$

where

$$\vec{D}(\vec{r}-\vec{r}')=-e(\vec{r}-\vec{r}')/|\vec{r}-\vec{r}'|^3\,. \qquad (6.2)$$

$\vec{D}(\vec{r}-\vec{r}')$ is the field produced at the point $\vec{r}$ by an electron at $\vec{r}'$. $\vec{P}(\vec{r})$ is the full polarization field of Eq. (4.3) since the electron interacts with both the ionic polarization and the electronic polarization resulting from this ionic polarization.

Fourier transforming Eq. (6.1) using

$$\frac{\vec{r}-\vec{r}'}{|\vec{r}-\vec{r}'|^3}=-\int d\vec{k}\,e^{i\vec{k}\cdot(\vec{\rho}-\vec{\rho}')}\,\frac{i\vec{K}}{2\pi k}\,e^{-k|z-z'|}\,, \qquad (6.3)$$

one finds

$$H'=-2\pi e\sum_{\vec{k}}e^{-i\vec{k}\cdot\vec{\rho}'}\int_{-a}^{+a}dz\,e^{-k|z-z'|}\vec{\chi}\cdot\vec{P}^{*}(\vec{k},z)\,, \qquad (6.4)$$

where $\vec{\chi}$ is the two-dimensional vector defined by LKB as

$$\vec{\chi}=(i/k)\,\vec{K}=[i,-\Theta(z-z')]\,. \qquad (6.5)$$

Making use of the expansion of $\vec{P}(\vec{k},z)$ in terms of the eigenvectors of Table I, we finally have

$$H'=-2\pi\sum_{\vec{k},m,p}e^{-i\vec{k}\cdot\vec{\rho}'}\Gamma_{mp}(k,z')\,(1-n\alpha\phi^{m}_{p})^{-1} \times[a_{m,p}(\vec{k})+a^{\dagger}_{m,p}(-\vec{k})]\,, \qquad (6.6)$$

with

$$\Gamma_{mp}(k,z')=\left(\frac{\hbar\omega_p^2 e^2}{8\pi A\omega_{m,p}}\right)^{1/2}\int_{-a}^{+a} dz\, e^{-k|z-z'|}\times\vec{\chi}\cdot\vec{\pi}_p^{*m}(\vec{k},z)\,. \qquad (6.7)$$

H' above is identical to the interaction operator of LKB except for the factor $(1/2\pi)(1-n\alpha\phi_p^m)^{-1}$ and the fact that $\omega_{m,p}$ as defined by Eqs. (4.20), (4.23a), and (4.23b) is dependent on α.

To find the operator describing the interaction between the electron and the LO phonons, we write ω_p^2 (which is defined as $4\pi ne^2/\mu$ and therefore independent of α) in terms of $\omega_{\rm LO}^2$, $\omega_{\rm TO}^2$, and α, that is,

$$\omega_p^2=(\omega_{\rm LO}^2-\omega_{\rm TO}^2)(1+\tfrac{8}{3}\pi n\alpha)(1-\tfrac{4}{3}\pi n\alpha)\,. \qquad (6.8)$$

Then for the LO modes, the constant factor in H' is

$$2\pi\left(\frac{\hbar\omega_p^2 e^2}{8\pi A\omega_{\rm LO}}\right)^{1/2}(1+\tfrac{8}{3}\pi n\alpha)^{-1}=\left[\frac{\pi e^2\hbar\omega_{\rm LO}}{2A}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]^{1/2}, \qquad (6.9)$$

where we have used the Clausius-Mossotti relation

$$\epsilon_\infty=1+4\pi n\alpha/(1-\tfrac{4}{3}\pi n\alpha)\,. \qquad (6.10)$$

Since, as LKB have shown, the integral in Eq. (6.7) for the LO modes is

$$\int_{-a}^{+a} dz\, e^{-k|z-z'|}\vec{\chi}\cdot\vec{\pi}_p^{*m}(\vec{k},z)=\frac{2\sqrt{a}}{(k^2a^2+\frac{1}{4}m^2\pi^2)^{1/2}}\begin{cases}\cos(m\pi/2a)z\,, & m=1,3,\ldots,\\ \sin(m\pi/2a)z\,, & m=2,4,\ldots;\end{cases} \qquad (6.11)$$

the electron–LO-phonon interaction operator is given by

$$H'_{\rm LO}=\left[\frac{4\pi e^2}{V}\hbar\omega_{\rm LO}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]^{1/2}\sum_{\vec{k}}e^{-i\vec{k}\cdot\vec{\rho}'}\left(\sum_{m=1,3\ldots}\frac{\cos(m\pi/2a)z}{[k^2+(m\pi/2a)^2]^{1/2}}\,[a_{m+}(\vec{k})+a_{m+}^\dagger(-\vec{k})]+\sum_{m=2,4\ldots}\frac{\sin(m\pi/2a)z}{[k^2+(m\pi/2a)^2]^{1/2}}\,[a_{m-}(\vec{k})+a_{m-}^\dagger(-\vec{k})]\right). \qquad (6.12)$$

We will show in the Appendix that for a very thick slab $H'_{\rm LO}$ becomes equivalent to the bulk Fröhlich Hamiltonian.

For the operator describing the interaction between the electron and the SO modes we write

$$(1-n\alpha\phi_\pm^0)=[\tfrac{3}{2}/(\epsilon_\infty+2)][(\epsilon_\infty+1)\mp(\epsilon_\infty-1)e^{-2ka}]\,, \qquad (6.13)$$

and express ω_p^2 in the more convenient form

$$\omega_p^2=9\omega_{\rm TO}^2(\epsilon_0-\epsilon_\infty)/(\epsilon_\infty+2)^2\,. \qquad (6.14)$$

For the SO modes, the integral in Eq. (6.7) is

$$\int_{-a}^{+a} dz\, e^{-k|z-z'|}\,\vec{\chi}\cdot\vec{\pi}_\pm^{0*}(\vec{k},z)=\left(\frac{\sinh 2ka}{k}\right)^{1/2}e^{-ka}\begin{cases}\cosh kz'/\cosh ka\,, & p=+\,,\\ \sinh kz'/\sinh ka\,, & p=-\,,\end{cases} \qquad (6.15)$$

so that the interaction operator $H'_{\rm SO}$ can be written

$$H'_{\rm SO}=-\left(\frac{2\pi e^2\hbar\omega_{\rm TO}}{A}(\epsilon_0-\epsilon_\infty)\right)^{1/2}\sum_{\vec{k}}e^{-i\vec{k}\cdot\vec{\rho}'}\left(\frac{\sinh 2ka}{k}\right)^{1/2}e^{-ka}\{G_+(k,z')[a_{0+}(\vec{k})+a_{0+}^\dagger(-\vec{k})]+G_-(k,z')[a_{0-}(\vec{k})+a_{0-}^\dagger(-\vec{k})]\}\,. \qquad (6.16)$$

In the above equation we have defined

$$G_+(k,z')=\frac{\cosh kz'/\cosh ka}{(\epsilon_\infty+1)-(\epsilon_\infty-1)e^{-2ka}}\times\left(\frac{(\epsilon_\infty+1)-(\epsilon_\infty-1)e^{-2ka}}{(\epsilon_0+1)-(\epsilon_0-1)e^{-2ka}}\right)^{1/4} \qquad (6.17a)$$

and

$$G_-(k,z')=\frac{\sinh kz'/\sinh ka}{(\epsilon_\infty+1)+(\epsilon_\infty-1)e^{-2ka}}\times\left(\frac{(\epsilon_\infty+1)+(\epsilon_\infty-1)e^{-2ka}}{(\epsilon_0+1)+(\epsilon_0-1)e^{-2ka}}\right)^{1/4}. \qquad (6.17b)$$

When $\alpha=0$ $(\epsilon_\infty=1)$, the above operators reduce to $1/2\pi$ times the corresponding operator of LKB. This factor of $1/2\pi$ is due to the difference in the definition of the Fourier transform, and in the conversion from sums to integrals, as used by LKB and in this paper.

VII. EXTERNAL-ELECTRON PROBLEM

In this section we consider the interaction of a classical electron outside the slab with the polarization eigenmodes. The interaction operator H' is again that of Eq. (6.6), where now the integral in $\Gamma_{mp}(k,z')$ is calculated for an electron at $z'=R+a$, where R is the distance from the surface at $+a$ to the electron outside. Since the electric field produced by the LO phonons is zero outside the slab, the electron interacts only with the surface modes. Then H' is written

$$H' = -\left(\frac{\pi\hbar e^2}{2A}(\epsilon_0-\epsilon_\infty)\right)^{1/2}\frac{3\omega_{\mathrm{TO}}}{\epsilon_\infty+2} \times\sum_{\vec{\mathrm{k}}} e^{-i\vec{\mathrm{k}}\cdot\vec{\rho}'}\left(\frac{\sinh 2ka}{k}\right)^{1/2} e^{-kz'} \times\sum_{p=\pm}(1-n\alpha\phi_p^0)^{-1}\omega_{0,p}^{-1/2}[a_{0,p}(\vec{\mathrm{k}})+a_{0,p}^{\dagger}(-\vec{\mathrm{k}})]. \tag{7.1}$$

We consider the electron to be fixed at $\vec{\mathrm{r}}=(0,z')$ and we calculate the second-order perturbation-theory energy of interaction, where we assume that the electron does not recoil during the emission or absorption of an SO phonon. The result is

$$\Delta E^{(2)} = -e^2(\epsilon_0-\epsilon_\infty) \times\int_0^\infty dk\, e^{-2kR}\frac{(1-e^{-4ka})(a_1+b_1e^{-4ka})}{(a_2+b_2e^{-4ka})(a_3+b_3e^{-4ka})}, \tag{7.2}$$

where

$$\begin{aligned} &a_1=(\epsilon_0+1)(\epsilon_\infty+1), && b_1=(\epsilon_0-1)(\epsilon_\infty-1),\\ &a_2=(\epsilon_0+1)^2, && b_2=-(\epsilon_0-1)^2,\\ &a_3=(\epsilon_\infty+1)^2, && b_3=-(\epsilon_\infty-1)^2. \end{aligned} \tag{7.3}$$

The integration in $\Delta E^{(2)}$ can be performed analytically, but the result is rather cumbersome and not very instructive. We consider instead the simpler and more interesting case of a semi-infinite medium, that is, we let $a\to\infty$ in $\Delta E^{(2)}$. We then immediately find that

$$\Delta E^{(2)} = -(e^2/2R)(\epsilon_0-\epsilon_\infty)/(\epsilon_0+1)(\epsilon_\infty+1). \tag{7.4}$$

This is the interaction energy of an electron and the polarization eigenmodes of a semi-infinite dielectric medium when the electron is a distance R from the surface. We point out that this result includes the interaction with both the ionic polarization and the electronic polarization produced by the ionic motion.

To show that the result of Eq. (7.4) is the correct one, let us consider from the point of view of classical electrostatics the energy of interaction of a charge e and a semi-infinite dielectric medium. From the method of image charges one finds[10]

$$\Delta E = -(e^2/4R)(\epsilon-1)/(\epsilon+1), \tag{7.5}$$

where ϵ is the dielectric constant of the medium. Setting $\epsilon=\epsilon_0$ in ΔE would give the energy of interaction of the electron with the ionic polarization and with the electronic polarization due to both the ionic motion and the electron itself. Since we do not include this latter contribution to the electronic polarization in $\Delta E^{(2)}$, we must write for the classical result ΔE,

$$\Delta E = -\frac{e^2}{4R}\left(\frac{\epsilon_0-1}{\epsilon_0+1}-\frac{\epsilon_\infty-1}{\epsilon_\infty+1}\right). \tag{7.6}$$

ΔE above is therefore identical to $\Delta E^{(2)}$ of Eq. (7.4).

VIII. SUMMARY AND CONCLUSIONS

We have derived in this paper the eigenvectors and the eigenfrequencies of the optical polarization field in a dielectric slab, and the Hamiltonian describing the interaction of this polarization field with a free conduction electron. In particular, we have included the effect of that part of the electronic polarization due to the ionic motion.

To show the correctness of the electron-SO phonon interaction operator, we considered the interaction energy of a classical electron external to the slab and the SO polarization field. The energy found in this way is identical to the result gotten from the classical theory of image charges. In the case of the LO phonons we have shown that in the limit when the slab thickness is very large, the electron-LO phonon interaction operator of Sec. VI is equivalent to the interaction operator of the bulk Fröhlich Hamiltonian.

We conclude by considering how the inclusion of the electronic polarizability in the interaction Hamiltonians affects some previous results, for example, those of Ref. 4 (referred to as EM). In that work, EM calculated the energy of an electron bound near the surface of a semi-infinite crystal, when the electron interacts with both the bulk LO and the SO phonons. They found very shallow binding, with no binding at all for LO-phonon coupling constants greater than about two. In this geometry our interaction Hamiltonians, Eqs. (6.12) and (6.16), differ from those of EM by numerical factors alone. Taking these numerical factors into account we find that, owing to ϵ_∞ being set equal to unity, EM overestimated the electron-LO phonon interaction by a factor of three and the electron-SO phonon interaction by a factor of about 1.5. Therefore, the effect of the SO phonons will be greater than that accounted for by EM, giving a binding energy that will be deeper, and that will extend to coupling constants greater than 2. It appears then that the effect of the SO phonons on electron surface state formation in semiconductors may be greater than previously expected.

APPENDIX

In this section we show the equivalence of H'_{LO} of Eq. (6.12) and the electron-bulk LO-phonon interaction operator of the Fröhlich Hamiltonian. This interaction operator can be written

$$H'_{\mathrm{Fr}} = \sum_{\vec{\mathrm{K}}} V_K e^{-i\vec{\mathrm{K}}\cdot\vec{\mathrm{r}}}(a_K + a^\dagger_{-K}) , \qquad \text{(A1)}$$

where $\vec{\mathrm{K}}$ is a three-dimensional wave vector defined by $\vec{\mathrm{K}} = (\vec{\mathrm{k}}, k_z)$, and

$$V_K = \left[\frac{2\pi e^2 \hbar\omega_{\mathrm{LO}}}{VK^2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\right]^{1/2} . \qquad \text{(A2)}$$

If we split the sum over $\vec{\mathrm{K}}$ into a sum over $\vec{\mathrm{k}}$ and a sum over $k_z > 0$, H'_{Fr} becomes

$$H'_{\mathrm{Fr}} = \sum_{\vec{\mathrm{k}}, k_z > 0} V_K e^{-i\vec{\mathrm{k}}\cdot\vec{\rho}}\left[e^{-ik_z z}(a_{\vec{\mathrm{k}}, k_z} + a^\dagger_{-\vec{\mathrm{k}}, -k_z}) + e^{ik_z z}(a_{\vec{\mathrm{k}}, -k_z} + a^\dagger_{-\vec{\mathrm{k}}, k_z})\right] . \qquad \text{(A3)}$$

Writing the exponentials in terms of sine and cosine, we arrive at

$$H'_{\mathrm{Fr}} = \sqrt{2} \sum_{\vec{\mathrm{k}}, k_z > 0} V_K e^{-i\vec{\mathrm{k}}\cdot\vec{\rho}}\{\cos k_z z\,[a_+(\vec{\mathrm{k}}) + a^\dagger_+(-\vec{\mathrm{k}})] + \sin k_z z\,[a_-(\vec{\mathrm{k}}) + a^\dagger_-(-\vec{\mathrm{k}})]\} , \qquad \text{(A4)}$$

where

$$a_+(\vec{\mathrm{k}}) = (1/\sqrt{2}\,)(a_{\vec{\mathrm{k}}, k_z} + a_{\vec{\mathrm{k}}, -k_z}) \qquad \text{(A5a)}$$

and

$$a_-(\vec{\mathrm{k}}) = (-i/\sqrt{2}\,)(a_{\vec{\mathrm{k}}, k_z} - a_{\vec{\mathrm{k}}, -k_z}) . \qquad \text{(A5b)}$$

The operators $a^\dagger_+(-\vec{\mathrm{k}})$ and $a^\dagger_-(-\vec{\mathrm{k}})$ follow by the definition of the adjoint. The above operators describe phonons propagating as plane waves in two dimensions (in the direction of $\vec{\mathrm{k}}$) and as standing waves in the $\hat{z}$ direction.

In considering the Fröhlich Hamiltonian, which treats an electron interacting with the LO phonons in an infinite crystal, one imposes Born–von Karmon or periodic boundary conditions on the electron and phonon wave functions. Of course, all physical quantities are independent of the boundary conditions one uses. Since we want to compare H'_{Fr} to H'_{LO} describing the same interaction but in a crystal slab with surfaces at $\pm a$ (we assume a is very large, approaching infinity, so that the electron is always far from the surface), we will impose on Eq. (A4) the boundary conditions that $\sin k_z z$ and $\cos k_z z$ vanish at $z = \pm a$. From the analysis of Sec. III, this can be seen to be equivalent to the requirement that the potential due to the LO phonons vanish at $\pm a$, a condition which does hold for the LO phonons in the slab. It is then easily seen that H'_{Fr} above becomes identical to H'_{LO} of Eq. (6.12).

---

*Work performed in the framework of the joint project E. S. I. S. (Electronic Structure in Solids) of the University of Liège and the University of Antwerpen, Belgium.

†Present address: Dept. of Physics, University of Delaware, Newark, Del. 19711.

[1] R. Fuchs and K. L. Kliewer, Phys. Rev. 140, A2076 (1965).

[2] A. A. Lucas, E. Kartheuser, and R. G. Badro, Phys. Rev. B 2, 2488 (1970).

[3] S. Q. Wang and G. D. Mahan, Phys. Rev. B 6, 4517 (1972).

[4] E. Evans and D. L. Mills, Solid State Commun. 11, 1093 (1972); Phys. Rev. B 8, 4004 (1973).

[5] T. Fujiwara and K. Ohtaka, J. Phys. Soc. Jpn. 24, 1326 (1968).

[6] John David Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), p. 101.

[7] H. Fröhlich and N. F. Mott, Proc. R. Soc. Lond. A 171, 496 (1939).

[8] See, for example, the treatment by Charles Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1968), p. 380.

[9] H. Fröhlich, Adv. Phys. 3, 325 (1954).

[10] John David Jackson, in Ref. 6, p. 110.