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Theory of Inelastic Scattering of Slow Electrons by Long-Wavelength Surface of Optical Phonons: Multiphonon Processes*

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We describe a quantum-mechanical theory of the inelastic scattering of low-energy electrons by multiphonon processes, from the surface of a semi-infinite crystal. A model introduced in an earlier paper is also employed in this work. The model describes the interaction of an incident low-energy electron with surface optical phonons by means of the macroscopic electric field set up outside the crystal by the ion motion. The model may be used to describe scattering either from ionic crystals, such as ZnO, or from nonionic crystals. In this paper, we find an explicit expression for the wave function of the outgoing electron, and we obtain an expression for the probability that n phonons are created or absorbed in the scattering process. Two cases are considered. First we examine the cross section for scattering off thermal phonons, and second from a coherent surface wave excited by external means. For the first case, our result agrees with the earlier semiclassical theory of Lucas and Sunjic. However, the model here is more general than theirs, since it is fully quantum mechanical. We show explicitly that the energy-loss cross section is proportional to the intensity of the specular beam, for scattering off both ionic and covalent crystals. For the second case (scattering from surface optical phonons generated coherently by an external source), we obtain a closed expression for the cross section. The physical origin of differences between the expressions is discussed.

I. INTRODUCTION

The study of the inelastic scattering of low-energy electrons by phonons from crystal surfaces provides a powerful method for the study of the vibrational properties of the surface region, in principle. However, until recently, it has proved difficult to carry out such measurements, primarily because it has proved difficult to produce electron beams sufficiently monoenergetic so the energy spread of the incoming electrons is small compared to phonon energies. However, Propst and Piper[1] reported an experimental study of the inelastic scattering of electrons by vibrational motions of hydrogen and other molecular species absorbed on a tungsten surface. More recently, Ibach has studied surface optical phonons on the surface of the ionic crystal ZnO,[2] and on the (111) surface of silicon[3] by means of inelastic low-energy electron scattering.

In the case of ZnO, it is clear from the data that the scattering is produced by the interaction of the electron beam with the macroscopic electric field set up outside the crystal by the ion motion. This is so because the inelastically scattered electrons have an angular distribution sharply peaked about the specular direction. The absolute scattering intensity, the dependence of the inelastic-scattering cross section on incident electron energy and on the number of phonons created in the scattering process are in remarkable agreement with the semiclassical theory of Lucas and Sunjic.[4,5] In the theory of Lucas and Sunjic, the electron is treated as a classical point particle which moves along the specular trajectory, at constant speed. The electric field of the electron excites the surface optical modes (Fuchs-Kliewer modes[6]) of the ionic crystal. Lucas and Sunjic calculate the energy transferred to the surface modes, by a method which takes due account of the quantized character of the surface modes.

The data obtained on the silicon surface are intriguing, in that the inelastics emerge with an angular distribution that is also narrowly peaked about the specular direction. This means that even though the atoms in the bulk have a dynamic or dipole-moment effective charge of zero, the atoms in or near the surface layer have a nonzero effective charge. This is presumably because the atoms very close to the surface feel the absence of an in-

version center in the crystal.

In an earlier paper, [7] the present authors discussed a model which describes the interaction of the electron with the surface optical phonons in a nonionic crystal such as silicon. In the model, the electron is treated in a quantum-mechanical fashion, in the sense that the cross section for inelastic scattering of the electron by the surface optical modes is obtained from the solution of the Schrödinger equation. Actually, the model can be directly applied to the ionic crystal by the appropriate choice of the parameter $\Delta(Q_{\parallel})$, to use our previous notation.

In the introductory section of the previous paper, we raised some objections to the physical picture employed by Lucas and Sunjic. One may feel that the classical theory should be valid since the de Broglie wavelength of the electron is small compared to that of the optical phonons which play the dominant role in the scattering. In this limit, one may think of a picture in which the incident particle is described by a well-localized wave packet, with spatial extent small compared to the surface phonon wavelength. Then the classical point-particle picture is an appropriate one. However, one point which brings this argument into question is that the incident electron beam is highly monochromatic. The energy spread of the electrons in the beam is so small that the smallest wave packet one can construct is the order of several surface-phonon wavelengths in spatial extent. In this circumstance, it seemed to us that one ought to describe the scattering process in fully quantum-mechanical terms, by means of the Schrödinger equation. This has the advantage that the kinematical aspects of the scattering process (such as conservation of wave-vector components in the plane parallel to the surface) enter quite naturally, and a proper description of the reflection of the electron off the crystal surface is obtained. Both of these features are not included in the semiclassical description.

In our previous work, [7] we introduced a simple model which may be used to obtain a quantum-mechanical description of the scattering of low-energy electrons from the crystal surface by surface optical phonons, for the case where the scattering is produced by the field set up outside the crystal by the ion motion. We obtained an expression for the total cross section and the angular distribution of electrons scattered by surface optical phonons. The theory could be applied either to ionic crystals such as ZnO, or covalent crystals such as Si. In this work, we examined only the theory of one-phonon processes, in which the electron is scattered by emitting or absorbing a single surface optical phonon. When our results were applied to ionic crystals, we recovered an expression for this case equivalent to that obtained earlier by Lucas and Sunjic.

Thus, as far as the total cross section associated with one-phonon scatterings is concerned, there appears to be no discrepancy between the results of our quantum-mechanical theory, and the semiclassical theory of Lucas and Sunjic, even though we raised questions about the validity of the physical picture employed by these authors. It is important to know if this is a feature of only the lowest-order processes, or if our quantum-mechanical model provides predictions identical to those of Lucas and Sunjic for multiphonon processes as well. We should point out that energy-loss peaks associated with the creation of several surface optical phonons are observed in ZnO, [2] and the Lucas-Sunjic theory gives an excellent account of the relative intensity of these peaks. [4,5] In this paper, we demonstrate that our model provides the same expression as the Lucas-Sunjic theory for the energy-gain or energy-loss cross section associated with multiphonon scatterings from thermal phonons. For reasons discussed above, our model does give a more complete description of the scattering process. For example, we can see quite directly that the cross section for creating (or absorbing) an arbitrary number n of surface optical phonons is proportional to the intensity of the specularly reflected beam.

We also consider the form of the cross section for energy loss or gain associated with the scattering of a low-energy electron from a coherently generated surface-optical-phonon wave. Here we do obtain an expression distinctly different from that provided by the semiclassical Lucas-Sunjic theory. The contribution to the cross section from processes of higher than first order depends on the fact that the electron wave at the time of a given scattering carries with it information about the phase of the coherent wave gained from previous scatterings. A wave-mechanical picture of the electron is required to include this feature into the theory.

The discussion in this Introduction has been concerned entirely with the small-angle inelastic scattering produced by the macroscopic electric field set up outside the crystal by the ion motion. We should point out that low-energy electrons may also scatter inelastically from phonons by interacting with the ion cores. These scattering processes deflect the electrons through a large angle. The experimental study of the electrons inelastically scattered by phonons through large angles has the potential of providing very detailed information about the lattice dynamics of the surface layers of the crystal. Such an experiment would be a study of the energy spectrum of electrons that form the thermal diffuse background. The theory of large-angle inelastic scattering by phonons, along with a

discussion of the lattice-dynamical information one may obtain by such a study, has been discussed recently by Roundy and Mills.[8]

The organization of this paper is the following. In Sec. II, we write down the Schrödinger equation for the model of the interactions of the incident electron with surface optical phonons we considered earlier. Then by a study of the structure of the perturbation series obtained by repeated iteration of the equation, we obtain an explicit form for the wave function of the outgoing electron. The wave function is valid for arbitrary values of the electron surface-optical-phonon coupling strength, and the result is valid so long as the electric field set up by the surface phonons varies slowly in space on the scale of the electron's de Broglie wavelength, and slowly in time compared to $\hbar/E^{(0)}$, where $E^{(0)}$ is the energy of the incident electron. In Sec. III, we consider first a simple closely related physical situation where a very similar form for the wave function is readily obtained by analytic means. Then in Sec. III we obtain an expression for the cross section for scattering with energy loss or gain from thermal phonons. We show here that our model gives the same result for the cross section as the Lucas-Sunjic theory. In Sec. IV, we discuss the interaction of an electron with a coherently generated surface optical wave.

II. GENERAL THEORY

We begin this section by recalling the properties of the model employed in the earlier work. Consider an electron incident on a semi-infinite crystal. The surface of the crystal lies in the x-y plane, and the crystal occupies the lower half-space $z<0$. Suppose the atoms are regarded as fixed at their equilibrium position. The electron is then Bragg scattered (elastically) from the surface region, which is periodic in the two directions parallel to the surface. We take $V_0(\vec{x})$ to be the potential appropriate to the semi-infinite crystal. In this paper, we follow the procedure we employed earlier, and we take for $V_0(\vec{x})$ the simple step potential

$$V_0(\vec{x}) = V_0\,\theta(-z)\,, \tag{1}$$

where

$$\theta(x) = \begin{cases} 1\,, & x>0 \\ 0\,, & x<0\,. \end{cases}$$

The parameter V_0 will be taken to be complex, with the physical origin of the imaginary part in the presence of electron-electron interactions which attenuate the incident beam within a mean free path of the crystal surface. The simple form for $V_0(\vec{x})$ represents a severe idealization of the actual state of affairs. However, with the ansatz in Eq. (1), we will greatly simplify the discussion that follows. The electric field outside the crystal set up by the lattice vibrations which is ultimately responsible for the inelastic scattering considered here has a rather long range, the order of 100 Å or so, for a typical surface optical phonon. The inelastic-scattering events thus occur rather far from the crystal surface, if we measure distances in units of the lattice constant, so we feel the general structure of the inelastic-scattering cross section should not depend on the precise form of $V_0(\vec{x})$. Our ansatz for $V_0(\vec{x})$ leads to the presence of a specularly reflected beam, but to no Bragg scattering. All of the inelastic-scattering experiments to date have involved electrons scattered only a small angular distance from the specular beam, so the model gives an adequate description of this sort of scattering. The reflection coefficient $|R|^2$ for specular reflection from the surface is less than unity for our model, by virtue of the imaginary part of V_0. By treating V_0 as a phenomenological parameter, the intensity and energy dependence of the specular beam associated with scattering from the rigid lattice may be adjusted to a particular set of data.

Now suppose the lattice vibrates, by virtue of surface optical phonons that propagate along the surface. The effect of the lattice vibrations is to generate an electric field outside the crystal. We describe this field by introducing a time-dependent potential V_p into the Schrödinger equation of the crystal. We confine our attention to the case where scattering is produced by long-wavelength surface optical modes, with frequency ω_s independent of the wave vector $\vec{Q}_\parallel$ of the surface phonon parallel to the surface. In our earlier work, we discussed the form of V_p for surface optical phonons (Fuchs-Kliewer modes) on the surface of an ionic crystal and for surface phonons on a nonionic crystal such as silicon. In both cases, we found that V_p has the form

$$V_p = e^{i\omega_s t}\sum_{\vec{Q}_\parallel} \Delta(\vec{Q}_\parallel)\, e^{i\vec{Q}_\parallel\cdot\vec{x}_\parallel}\, e^{-Q_\parallel|z|} + \text{c. c.}\,, \tag{2}$$

where for each of the two cases, the explicit form of $\Delta(\vec{Q}_\parallel)$ has been given earlier. We shall not need the explicit form of $\Delta(\vec{Q}_\parallel)$ here. In Eq. (2), the sum over $\vec{Q}_\parallel$ is over the two-dimensional Brillouin zone appropriate to the surface layer of the crystal. Throughout the paper, the subscript $\parallel$ will be used to denote either a vector which lies in a plane parallel to the surface layer, or the projection of a general vector onto the plane parallel to the surface.

One comment about the quantity $\Delta(\vec{Q}_\parallel)$ is important. The coefficients $\Delta(\vec{Q}_\parallel)$, and $\Delta^*(\vec{Q}_\parallel)$ are directly proportional to the annihilation and creation operator $a_{\vec{Q}_\parallel}$ and $a^\dagger_{\vec{Q}_\parallel}$ associated with the surface mode. Thus, strictly speaking, V_p is not a c number, but an operator. In the main body of our dis-

cussion, we follow our earlier approach and treat $a_{\vec{Q}_\parallel}$ and $a^\dagger_{\vec{Q}_\parallel}$ simply as classical c-number normal-mode amplitudes. This method gives the correct expression for the cross section in the high-temperature region $kT \gg \hbar\omega_s$, where the quantized character of the surface phonons plays no essential role. We make the transition to the case of general temperatures by use of the correspondence principle, as we did earlier. By treating $\Delta(\vec{Q}_\parallel)$ and $\Delta^*(\vec{Q}_\parallel)$ as c numbers, we simplify intermediate steps in the discussion, without sacrificing any essential aspect of the physics. The correspondence principle allows us to construct the fully quantum-mechanical result at the end.

With these remarks in mind, the Schrödinger equation becomes (in units with $\hbar = 1$)

$$\left(-\frac{\nabla^2}{2m} + V_0\,\theta(-z) + \sum_{\vec{Q}_\parallel} \Delta(\vec{Q}_\parallel)\, e^{i\vec{Q}_\parallel\cdot\vec{x}_\parallel} e^{-Q_\parallel|z|} e^{i\omega_s t} + \sum_{\vec{Q}_\parallel} \Delta^*(\vec{Q}_\parallel)\, e^{-i\vec{Q}_\parallel\cdot\vec{x}_\parallel} e^{-Q_\parallel|z|} e^{-i\omega_s t}\right)\psi(\vec{x}, t) = i\,\frac{\partial\psi}{\partial t}(\vec{x}, t)\,. \quad (3)$$

At this point, it is convenient to perform a Fourier expansion with respect to the time variable, and a partial Fourier transform with respect to the spatial coordinate:

$$\psi(\vec{x}, t) = \int \frac{d^2k_\parallel\, d\omega}{(2\pi)^3}\, \psi(\vec{k}_\parallel, \omega; z)\, e^{i\vec{k}_\parallel\cdot\vec{x}_\parallel} e^{-i\omega t}\,; \quad (4)$$

then Eq. (3) may be rearranged to read

$$\left(\frac{k_\parallel^2}{2m} - \omega - \frac{1}{2m}\,\frac{\partial^2}{\partial z^2} + V_0\,\theta(-z)\right)\psi(\vec{k}_\parallel, \omega; z)$$

$$= -\sum_{\vec{Q}_\parallel} \Delta(\vec{Q}_\parallel)\, e^{-Q_\parallel|z|}\, \psi(\vec{k}_\parallel - \vec{Q}_\parallel; \omega - \omega_s)$$

$$-\sum_{\vec{Q}_\parallel} \Delta^*(\vec{Q}_\parallel)\, e^{-Q_\parallel|z|}\, \psi(\vec{k}_\parallel + \vec{Q}_\parallel; \omega + \omega_s)\,. \quad (5)$$

We next rewrite Eq. (5) in integral form by introducing the Green's function which satisfies

$$\left(-\frac{1}{2m}\,\frac{\partial^2}{\partial z^2} + \frac{k_\parallel^2}{2m} - \omega + V_0\,\theta(-z)\right) G(\vec{k}_\parallel, \omega; zz')$$

$$= \delta(z - z')\,, \quad (6)$$

and which is subject to the boundary conditions appropriate to the scattering problem. Explicitly, for fixed z', $G(\vec{k}_\parallel \omega; zz') \to 0$ as $z \to -\infty$, and $G(\vec{k}_\parallel \omega; zz')$ is subject to an outgoing wave boundary condition as $z \to +\infty$. With the use of the Green's function, Eq. (5) may be rewritten in the form of an integral equation. We have

$$\psi(\vec{k}_\parallel \omega; z) = \psi_0(\vec{k}_\parallel \omega; z) - \sum_{\vec{Q}_\parallel} \int_{-\infty}^{+\infty} dz'\, G(\vec{k}_\parallel \omega; zz')$$

$$\times \Delta(\vec{Q}_\parallel)\, e^{-Q_\parallel|z|}\, \psi(\vec{k}_\parallel - \vec{Q}_\parallel, \omega - \omega_s; z')$$

$$-\sum_{\vec{Q}_\parallel} \int_{-\infty}^{+\infty} dz'\, G(\vec{k}_\parallel \omega; zz')\, \Delta^*(\vec{Q}_\parallel)$$

$$\times e^{-Q_\parallel|z|}\, \psi(\vec{k}_\parallel + \vec{Q}_\parallel, \omega + \omega_s; z')\,. \quad (7)$$

In Eq. (7), the function $\psi_0(\vec{k}_\parallel \omega; z)$ is a solution to the differential equation (5) with $\Delta(\vec{Q}_\parallel)$ and $\Delta^*(\vec{Q}_\parallel)$ set equal to zero. This function describes the (elastic) scattering of an incident electron beam off the crystal surface. The explicit form of $\psi_0(\vec{k}_\parallel \omega; z)$ is readily obtained for our model. We shall ultimately need the function only in the region $z > 0$, outside the crystal. Let the incident electron beam have energy $E^{(0)}$ and wave vector $\vec{k}_{0\parallel}$ parallel to the surface. Define

$$k_{0z} = +\,(2mE^{(0)} - k_{0\parallel}^2)^{1/2}\,,$$

the wave-vector component of the incident electron beam normal to the surface. Then the explicit form of $\psi_0(\vec{k}_\parallel \omega; z)$ is, for $z > 0$,

$$\psi_0(\vec{k}_\parallel \omega; z) = (2\pi)^3\,\delta(\vec{k}_\parallel - \vec{k}_{0\parallel})\,\delta(\omega - E^{(0)})$$

$$\times (e^{-ik_{0z}z} + R_I\, e^{+ik_{0z}z})\,. \quad (8)$$

In Eq. (8), R_I is the reflection coefficient for specular reflection from the rigid crystal. For our model, R_I has the explicit form

$$R_I = (k_{0z} - i\gamma_0)/(k_{0z} + i\gamma_0)\,, \quad (9)$$

where

$$\gamma_0 = (k_{0\parallel}^2 - 2mE^{(0)} + 2m\,V_0)^{1/2}\,. \quad (9a)$$

In Eq. (9a), the choice of the square root is that which gives to γ_0 a positive real part.

Finally, we need the form of the Green's function which enters Eq. (7). This function is readily constructed explicitly from Eq. (6) and the associated boundary conditions. Define the quantities

$$\gamma = (k_\parallel^2 - 2m\omega + 2m\,V_0)^{1/2} \quad (10a)$$

and

$$k_z = (k_\parallel^2 - 2m\omega)^{1/2}\,, \quad (10b)$$

and also let

$$R = (k_z - i\gamma)/(k_z + i\gamma)\,,$$

$$T = 1 - R\,.$$

Again, γ is chosen to have a positive real part.

The Green's function is readily expressed in terms of two solutions of the homogeneous equation associated with Eq. (6). We denote these two functions as $\psi^-(\vec{k}_\parallel \omega; z)$ and $\psi^+(\vec{k}_\parallel \omega; z)$. Explicitly,

$$\psi^-(\vec{k}_\parallel \omega; z) = \begin{cases} e^{-ik_z z} + Re^{ik_z z}\,, & z > 0 \quad (11a) \\ Te^{+\gamma z}\,, & z < 0 \quad (11b) \end{cases}$$

and

$$\psi^+(\vec{k}_\parallel \omega; z) = \begin{cases} e^{+ik_z z}, & z > 0 \quad (12a) \\ \cosh\gamma z + i(k_z/\gamma)\sinh\gamma z, & z < 0. \quad (12b) \end{cases}$$

Then the Green's function has the form

$$G(\vec{k}_\parallel \omega; zz') = i\frac{m}{k_z}\left[\psi^+(\vec{k}_\parallel \omega; z)\,\psi^-(\vec{k}_\parallel \omega; z')\,\theta(z-z') + \psi^-(\vec{k}_\parallel \omega; z)\,\psi^+(\vec{k}_\parallel \omega; z')\,\theta(z'-z)\right]. \quad (13)$$

The equations displayed above allow us to study the scattering of an incident electron by surface optical phonons. We shall proceed by examining the form of the iterative solution to Eq. (7). In our earlier paper,[7] we considered the inelastic scattering produced by the one-phonon process. The amplitude of the scattered wave to lowest order in $\Delta(\vec{Q}_\parallel)$ is obtained by simply replacing the factors of $\psi(\vec{k}_\parallel \pm \vec{Q}_\parallel, \omega \pm \omega_s; z')$ on the right-hand side of Eq. (7) by the amplitude ψ_0 of the specular beam. The purpose of this paper is to study the contribution to the scattered wave from higher-order processes. We proceed by repeatedly iterating Eq. (7).

Before we begin, we mention one approximation used earlier that we also employ here. The phonons responsible for the principal part of the scattering have rather long wavelengths, the order of 100 Å or so.[4,7] The electric field set up by the phonon thus extends quite far into the vacuum outside the crystal. From the form of the interaction potential, which varies with space like $e^{i\vec{Q}_\parallel\cdot\vec{x}_\parallel}e^{-Q_\parallel|z|}$ for a phonon of wave $\vec{Q}_\parallel$, we see that the field extends a distance the order of the surface-optical-phonon wavelength into the vacuum. Because of the strong electron-electron scattering present in the medium (represented by the imaginary part of V_0 in our phenomenological potential), the electron wave is attenuated very rapidly as it enters the medium. The electron mean free path is expected to be small compared to typical values of $\vec{Q}_\parallel$.[9] In our formalism, this feature enters through the form of $\psi_0(\vec{k}_\parallel \omega; z)$, which is proportional to $e^{\gamma_0 z}$ for $z < 0$. The rapid attentuation of the electron beam into the crystal means that the integrations over z' which appear in Eq. (7) may be taken to extend only over the vacuum region $z' > 0$, where the electron waves have propagating character. The contribution from the crystal region $z' > 0$ is smaller than that from the vacuum region $z' > 0$ by the factor $\langle Q_\parallel\rangle/\gamma_0 \ll 1$, where $\langle Q_\parallel\rangle$ is the wave vector of those surface phonons which make the dominant contribution to the cross section. The earlier remarks indicate that $\langle Q_\parallel\rangle/\gamma_0$ is typically the order of 10^{-1}. Our calculation may be readily corrected to take account of the finite penetration of the electron beam into the crystal, if this is desired.

To begin, we first extract from Eq. (7) an expression for the amplitude of the scattered wave $\psi_s(\vec{k}_\parallel \omega; z)$ associated with an electron with wave vector $\vec{k}_\parallel$ parallel to the surface, and energy ω. With the remarks of the preceding paragraph in mind, we find

$$\psi_s(\vec{k}_\parallel \omega; z) = -\sum_{\vec{Q}_\parallel}\int_0^\infty dz'\, e^{-Q_\parallel z'}\, G(\vec{k}_\parallel \omega; zz') \times\left[\Delta(\vec{Q}_\parallel)\,\psi(\vec{k}_\parallel - \vec{Q}_\parallel, \omega - \omega_s, z') + \Delta^*(\vec{Q}_\parallel)\,\psi(\vec{k}_\parallel + \vec{Q}_\parallel; \omega + \omega_s; z')\right]. \quad (14)$$

We write

$$\psi_s(\vec{k}_\parallel \omega, z) = \sum_{n=1}^{\infty}\psi_s^{(n)}(\vec{k}_\parallel \omega z), \quad (15)$$

where $\psi_s^{(n)}(\vec{k}_\parallel \omega, z)$ is the contribution to the amplitude of the outgoing wave which is nth order in the magnitude of the coupling constant $\Delta(\vec{Q}_\parallel)$. One readily obtains a recursion relation between $\psi_s^{(n)}$ and $\psi_s^{(n-1)}$:

$$\psi_s^{(n)}(\vec{k}_\parallel \omega, z) = -\sum_{\vec{Q}_\parallel}\int_0^\infty dz'\, e^{-Q_\parallel z'}\, G(\vec{k}_\parallel \omega; zz') \times\left[\Delta(\vec{Q}_\parallel)\,\psi_s^{(n-1)}(\vec{k}_\parallel - \vec{Q}_\parallel, \omega - \omega_s, z') + \Delta^*(\vec{Q}_\parallel)\,\psi_s^{(n-1)}(\vec{k}_\parallel + \vec{Q}_\parallel, \omega + \omega_s, z')\right]. \quad (16)$$

Consider the explicit form of the contribution to the wave-function second order in $\Delta(\vec{Q}_\parallel)$. It is a short exercise to show that the *outgoing* wave ($z \to \infty$) has the form

$$\psi_s^{(2)}(\vec{k}_\parallel \omega, z) = -\frac{(2\pi)^3 m^2}{k_z}\, e^{ik_z z}\left(\sum_{\vec{Q}_\parallel \vec{Q}'_\parallel} \mathcal{J}_{s0}(Q_\parallel Q'_\parallel; k_z^{(I-)})\,\frac{\Delta(\vec{Q}_\parallel)}{k_z^{(I+)}}\left[\Delta(\vec{Q}'_\parallel)\,\delta(\omega - 2\omega_s - E^{(0)})\,\delta(\vec{k}_\parallel - \vec{Q}_\parallel - \vec{Q}'_\parallel - \vec{k}_0) + \Delta^*(\vec{Q}'_\parallel)\,\delta(\omega - E^{(0)})\,\delta(\vec{k}_\parallel - \vec{Q}_\parallel + \vec{Q}'_\parallel - \vec{k}_{0\parallel})\right] + \sum_{\vec{Q}_\parallel \vec{Q}'_\parallel} \mathcal{J}_{s0}(Q_\parallel Q'_\parallel; k_z^{(I+)})\,\frac{\Delta^*(\vec{Q}_\parallel)}{k_z^{(I-)}} \times\left[\Delta(\vec{Q}'_\parallel)\,\delta(\omega - E^{(0)})\,\delta(\vec{k}_\parallel + \vec{Q}_\parallel - \vec{Q}'_\parallel - \vec{k}_{0\parallel}) + \Delta^*(\vec{Q}'_\parallel)\,\delta(\omega + 2\omega_s - E^{(0)})\,\delta(k_\parallel + Q_\parallel + Q'_\parallel - k_{0\parallel})\right]\right). \quad (17)$$

While Eq. (17) has a rather complex structure, we shall see that it simplifies shortly. In this expression $k_z = (2m\omega - k_\parallel^2)^{1/2}$ is the normal component of the wave vector of the outgoing wave, $k_z^{(I\pm)}$ is the wave vector of an electron in an intermediate state, given explicitly by

$$k_z^{(I\pm)} = [2m(\omega \pm \omega_s) - (k_\parallel \pm Q_\parallel)^2]^{1/2} .$$

The quantity $\mathcal{I}_{s0}(Q_\parallel Q'_\parallel; k_z^{(I)})$ is an integral to be discussed below. The first and fourth terms of Eq. (17) describe a second-order inelastic process in which an electron scatters by absorbing or emitting two surface phonons, respectively. The second and third terms describe elastic scattering, in which the electron is deflected away from the specular direction by emission and subsequent absorption of a surface optical phonon, respectively. Note these processes produce an angular spread in the outgoing elastically scattered electrons.

The integral $\mathcal{I}_{s0}(\vec{Q}_\parallel \vec{Q}'_\parallel; k_z)$ is given by

$$\mathcal{I}_{s0}(Q_\parallel Q'_\parallel; k_z^{(I)}) = \int_0^\infty dz' \, (e^{-(Q_\parallel + ik_z)z'} + R_s e^{-(Q_\parallel - ik_z)z'}) \Big[\int_0^{z'} dz'' \, e^{ik_z^{(I)} z'} (e^{-ik_z^{(I)} z''} + R_I e^{+ik_z^{(I)} z''})$$

$$\times (e^{-(Q'_\parallel + ik_{0z})z''} + R_0 e^{-(Q'_\parallel - ik_{0z})z''}) + \int_{z'}^\infty dz'' (e^{-(Q'_\parallel + ik_{0z})z''} + R_0 e^{-(Q'_\parallel - ik_{0z})z''}) e^{ik_z^{(I)} z''} + (e^{-ik_z^{(I)} z'} + R_I e^{ik_z^{(I)} z'})\Big] .$$

In this expression, R_0 is the coefficient for specular reflection of the incident beam off the surface, R_I that for specular reflection of the electron off the surface while it is in the intermediate state, and R_S that for reflection of the electron off the surface while it is in the outgoing state. Explicit evaluation of the integrals is straightforward, and

$$\mathcal{I}_{s0}(Q_\parallel Q'_\parallel, k_z^{(I)}) = \frac{1}{Q_\parallel + ik_{0z} + ik_z^{(I)}} \left(\frac{1}{Q_\parallel + ik_z - ik_z^{(I)}} - \frac{1}{Q_\parallel + Q'_\parallel + ik_z + ik_z^{(I)}} + \frac{R_s}{Q_\parallel - ik_z - ik_z^{(I)}} - \frac{R_s}{Q_\parallel + Q'_\parallel - ik_z + ik_z^I} \right)$$

$$+ \frac{1}{Q'_\parallel + ik_{0z} - ik_z^{(I)}} \left(\frac{R_I}{Q_\parallel + ik_z - ik_z^{(I)}} + \frac{1}{Q_\parallel + Q'_\parallel + ik_{0z} + ik_z} + \frac{R_I R_s}{Q_\parallel - ik_z - ik_z^{(I)}} + \frac{R_s}{Q_\parallel + Q'_\parallel + ik_z^{(I)} - ik_z} \right)$$

$$+ \frac{1}{Q'_\parallel - ik_{0z} + ik_z^{(I)}} \left(\frac{R_0}{Q_\parallel + ik_z - ik_z^{(I)}} - \frac{R_0}{Q_\parallel + Q'_\parallel + ik_z - ik_z - ik_{0z}} + \frac{R_0 R_s}{Q_\parallel - ik_z - ik_z^{(I)}} - \frac{R_0 R_s}{Q_\parallel + Q'_\parallel - ik_z - ik_z^{(I)}} \right)$$

$$+ \frac{1}{Q'_\parallel - ik_{0z} - ik_z^{(I)}} \left(\frac{R_0 R_I}{Q_\parallel + ik_z - ik_z^{(I)}} + \frac{R_0 R_I R_s}{Q_\parallel - ik_z - ik_z^{(I)}} + \frac{R_0}{Q_\parallel + Q'_\parallel - ik_{0z} + ik_z} + \frac{R_0 R_s}{Q_\parallel + Q'_\parallel - ik_{0z} - ik_z} \right).$$

Even in second order, for the present surface scattering problem, the expression for the wave function is most cumbersome and unwieldly. Little progress can be made, so long as we retain the full form of the wave function for the higher-order processes. However, upon following the argument employed in our earlier study of first-order scattering, we find one approximation can be introduced which greatly simplifies the problem. As mentioned in the Introduction, the phonons which make the dominant contribution to the scattering have a wavelength long compared to the de Broglie wavelength of the electron. This means the quantities k_{0z}, $k_z^{(I)}$, and k_z are all very much greater than $Q_\parallel$ or $Q'_\parallel$. The dominant contribution to $\mathcal{I}_{s0}$ will then come from the three terms for which both denominators contain *differences* between two k_z's. For example, consider the two-phonon emission case, where $k_z^{(I)}$ is given by

$$k_z^{(I)} = [2m(\omega - \omega_s) - (k_\parallel - Q_\parallel)^2]^{1/2}$$

$$= [k_z^2 + 2(\vec{k}_\parallel \cdot \vec{Q}_\parallel - m\omega_s) + Q_\parallel^2]^{1/2}$$

$$\cong k_z + \frac{(\vec{k}_\parallel \cdot \vec{Q}_\parallel - m\omega_s)}{k_z} . \qquad (18)$$

The last statement is valid when $\vec{Q}_\parallel$ and ω_0 are small. Thus, the difference $k_z^{(I)} - k_z$ is proportional to the small quantities $\vec{Q}_\parallel$ and ω_s, while $k_z + k_z^{(I)} \approx 2k_{0z} \gg k_z^{(I)} - k_z$. If we retain only the three dominant terms, then $\mathcal{I}_{s0}(Q_\parallel Q'_\parallel, k_z^{(I)})$ becomes

$$\mathcal{I}_{s0}(Q_\parallel Q'_\parallel, k_z^{(I)}) = \frac{R_0}{(Q_\parallel + ik_z - ik_z^{(I)})(Q_\parallel + Q'_\parallel + ik_z - ik_{z0})}$$

$$+ \frac{1}{Q'_\parallel + ik_{z0} - ik_z^{(I)}} \left(\frac{R_I}{Q_\parallel + ik_z - ik_{Iz}} + \frac{R_s}{Q_\parallel + Q'_\parallel + ik_{0z} - ik_z} \right) .$$

In our earlier work,[7] we presented a discussion of the physical nature of the scattering processes ignored by this approximation.

We now write the denominators in the expression for $\mathcal{I}_{s0}$ in a simpler form, by making use of the expansion in Eq. (18). Note that $\vec{k}_\parallel = \vec{V}_\parallel/m$, where $\vec{V}_\parallel$ is the velocity of the scattered electron parallel to the surface and m the free electron mass, and $k_z = V_\perp/m$, where $V_\perp$ is the magnitude of the velocity of the scattered electron normal to the surface. Since we have already seen that small-angle scatterings give the dominant contribution to the wave function in second order, we can safely ignore the difference between $V_\parallel$ and $V_\perp$ for electrons in the incident, intermediate, or outgoing

states. Then for the two-phonon emission case,

$$Q_{\parallel}+i(k_z-k_z^{(I)})\cong Q_{\parallel}+i\left(\frac{\omega_s-\vec{Q}_{\parallel}\cdot\vec{V}_{\parallel}}{V_{\perp}}\right)\equiv\frac{\alpha_{Q_{\parallel}}}{V_{\perp}} \quad (19a)$$

and

$$Q'_{\parallel}+i(k_z^{(I)}-k_{0z})\cong Q'_{\parallel}-i\left(\frac{\omega_s-\vec{Q}'_{\parallel}\cdot\vec{V}_{\parallel}}{V_{\perp}}\right)\equiv\frac{\alpha^*_{Q'_{\parallel}}}{V_{\perp}} . \quad (19b)$$

The second-order contribution to the wave function may now be expressed entirely in terms of the $\alpha_{Q_{\parallel}}$'s:

$$\psi_s^{(2)}(\vec{k}_{\parallel}\omega,z)=(i)^2(2\pi)^3\,e^{ik_z z}\sum_{\vec{Q}_{\parallel}\vec{Q}'_{\parallel}}\Bigg[\Delta(\vec{Q}_{\parallel})\,\Delta(\vec{Q}'_{\parallel})\,\delta(\vec{k}_{\parallel}-\vec{Q}_{\parallel}-\vec{Q}'_{\parallel}-\vec{k}_{0\parallel})\,\delta(\omega-2\omega_s-E^{(0)})$$
$$\times\left(\frac{R_0}{\alpha_{Q_{\parallel}}(\alpha_{Q_{\parallel}}+\alpha_{Q'_{\parallel}})}+\frac{R_I}{\alpha_{Q_{\parallel}}\alpha^*_{Q'_{\parallel}}}+\frac{R_s}{\alpha^*_{Q'_{\parallel}}(\alpha^*_{Q_{\parallel}}+\alpha^*_{Q'_{\parallel}})}\right)\Bigg]+\Delta(Q_{\parallel})\,\Delta^*(Q'_{\parallel})\,\delta(\vec{k}_{\parallel}-\vec{Q}_{\parallel}+\vec{Q}'_{\parallel}-\vec{k}_{0\parallel})\,\delta(\omega-E^{(0)})$$
$$\times\left(\frac{R_0}{\alpha_{Q_{\parallel}}(\alpha_{Q_{\parallel}}+\alpha^*_{Q'_{\parallel}})}+\frac{R_I}{\alpha_{Q_{\parallel}}\alpha_{Q'_{\parallel}}}+\frac{R_s}{\alpha_{Q'_{\parallel}}(\alpha^*_{Q_{\parallel}}+\alpha_{Q'_{\parallel}})}\right)+\Delta^*(\vec{Q}_{\parallel})\Delta(\vec{Q}'_{\parallel})\,\delta(\vec{k}_{\parallel}+\vec{Q}_{\parallel}-\vec{Q}'_{\parallel}-\vec{k}_{0\parallel})\,\delta(\omega-E^{(0)})$$
$$\times\left(\frac{R_0}{\alpha^*_{Q_{\parallel}}(\alpha^*_{Q_{\parallel}}+\alpha_{Q'_{\parallel}})}+\frac{R_I}{\alpha^*_{Q_{\parallel}}\alpha^*_{Q'_{\parallel}}}+\frac{R_s}{\alpha_{Q'_{\parallel}}(\alpha_{Q_{\parallel}}+\alpha^*_{Q'_{\parallel}})}\right)+\Delta^*(\vec{Q}_{\parallel})\Delta^*(\vec{Q}'_{\parallel})\,\delta(\vec{k}_{\parallel}+\vec{Q}_{\parallel}+\vec{Q}'_{\parallel}-\vec{k}_{0\parallel})\,\delta(\omega-2\omega_0-E^{(0)})$$
$$\times\left(\frac{R_0}{\alpha^*_{Q_{\parallel}}(\alpha^*_{Q_{\parallel}}+\alpha^*_{Q'_{\parallel}})}+\frac{R_I}{\alpha^*_{Q_{\parallel}}\alpha^*_{Q'_{\parallel}}}+\frac{R_s}{\alpha_{Q'_{\parallel}}(\alpha_{Q_{\parallel}}+\alpha_{Q'_{\parallel}})}\right). \quad (20)$$

The result displayed in Eq. (20) looks very unlike the expressions that occur in the semiclassical Lucas-Sunjic theory, in the sense that in their theory, the transition probability for emission of two surface phonons, one of wave vector $\vec{Q}_{\parallel}$ and one of wave vector $\vec{Q}'_{\parallel}$, is the product of the one-phonon transition probabilities, to within an overall numerical factor. In Eq. (20) no such factorization is evident.

Since small-angle inelastic processes have already been observed to give the dominant contribution to $\psi_s^{(2)}$, we may set R_I and R_S equal to R_0, the reflection coefficient of the incident beam, without incurring further error. We then form a new expression for $\psi_2^{(s)}(\vec{k}_{\parallel}\omega,z)$ by interchanging the dummy variables $\vec{Q}_{\parallel}$ and $\vec{Q}'_{\parallel}$ on the right-hand side of Eq. (20), then adding the resulting form to Eq. (20), and dividing by a factor of 2. This procedure produces a much simpler result for $\psi_s^{(2)}$:

$$\psi_s^{(2)}(\vec{k}_{\parallel}\omega;z)=(i)^2\,\frac{(2\pi)^3}{2}\,R_0\,e^{ik_z z}\sum_{Q_{\parallel}Q'_{\parallel}}\{\Delta(\vec{Q}_{\parallel})\Delta(\vec{Q}'_{\parallel})\,\delta(\vec{k}_{\parallel}-\vec{Q}_{\parallel}-\vec{Q}'_{\parallel}-\vec{k}_{0\parallel})\,\delta(\omega-2\omega_s-E^{(0)})$$
$$+[\Delta(\vec{Q}_{\parallel})\,\Delta^*(\vec{Q}'_{\parallel})\,\delta(\vec{k}_{\parallel}-\vec{Q}_{\parallel}+\vec{Q}'_{\parallel}-\vec{k}_{0\parallel})+\Delta(\vec{Q}'_{\parallel})\,\Delta^*(\vec{Q}_{\parallel})\delta(\vec{k}_{\parallel}-\vec{Q}'_{\parallel}+\vec{Q}_{\parallel}-\vec{k}_{0\parallel})]\,\delta(\omega-E^{(0)})$$
$$+\Delta^*(\vec{Q}_{\parallel})\,\Delta^*(\vec{Q}'_{\parallel})\,\delta(\vec{k}_{\parallel}+\vec{Q}_{\parallel}+\vec{Q}'_{\parallel}-\vec{k}_{0\parallel})\,\delta(\omega+2\omega_s-E^{(0)})\}\left(\frac{\alpha_{Q_{\parallel}}+\alpha^*_{Q_{\parallel}}}{\alpha_{Q_{\parallel}}\alpha^*_{Q_{\parallel}}}\right)\left(\frac{\alpha_{Q'_{\parallel}}+\alpha^*_{Q'_{\parallel}}}{\alpha_{Q'_{\parallel}}\alpha^*_{Q'_{\parallel}}}\right). \quad (21)$$

If one recalls the form of $\alpha_{Q_{\parallel}}$, then

$$\frac{\alpha_{Q_{\parallel}}+\alpha^*_{Q_{\parallel}}}{\alpha_{Q_{\parallel}}\alpha^*_{Q_{\parallel}}}=\frac{2Q_{\parallel}V_{\perp}}{Q_{\parallel}^2V_{\perp}^2+(\vec{Q}_{\parallel}\cdot\vec{V}_{\parallel}-\omega_s)^2} . \quad (21a)$$

If we now transform the wave function in Eq. (21) back into coordinate space, a remarkably simple form for the second-order wave function is obtained. To obtain this form, the algebra is a bit tedious, but the result follows from Eq. (21) in a perfectly straightforward manner. Define the function $\theta(\vec{r},t)$ as follows:

$$\theta(\vec{r},t)=\sum_{\vec{Q}_{\parallel}}\frac{2V_{\perp}Q_{\parallel}}{V_{\perp}^2Q_{\parallel}^2+(\omega_s-\vec{V}_{\parallel}\cdot\vec{Q}_s)^2}$$
$$\times[\Delta(\vec{Q}_{\parallel})\,e^{i\vec{Q}\cdot\vec{r}}\,e^{-i\omega_s t}+\text{c. c.}]. \quad (22)$$

In this expression, the vector $\vec{Q}$ is given by

$$\vec{Q}=\vec{Q}_{\parallel}+\hat{z}\left(\frac{\vec{V}_{\parallel}\cdot\vec{Q}_{\parallel}-\omega_s}{V_{\perp}}\right) . \quad (22a)$$

If an electron absorbs a surface phonon of wave vector $\vec{Q}_{\parallel}$ parallel to the surface in a manner that conserves wave-vector components parallel to the

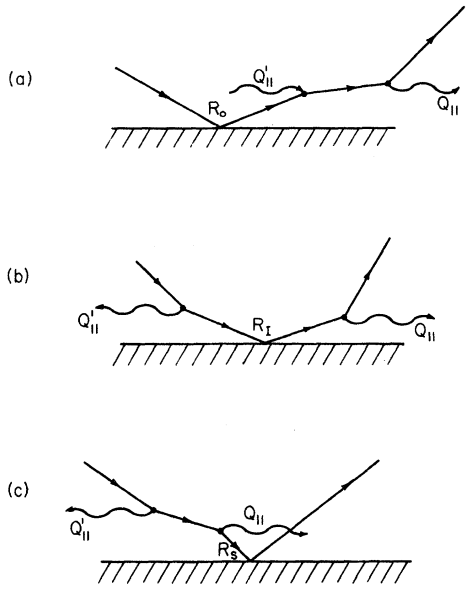

FIG. 1. Diagrammatic representation of some second-order scattering processes.

surface, along with energy, then $\vec{Q}$ is just the change in wave vector of the electron. In terms of the function $\theta(\vec{r}, t)$, the outgoing portion of the second-order wave function becomes, in coordinate space

$$\psi_s^2(\vec{r}, t) = R_0 \tfrac{1}{2}(i)^2 \theta^2(\vec{r}, t)\, e^{i\vec{k}_0\cdot\vec{r}} e^{-iE^{(0)}t} . \tag{23}$$

The quantity $R_0 e^{i\vec{k}_0\cdot\vec{r}-iE^{(0)}t}$ in Eq. (23) is just the outgoing portion of the specular beam, elastically scattered off the rigid crystal with reflection coefficient R_0. The amplitude of the outgoing wave to second order in the electron-phonon coupling parameter $\Delta(\vec{Q}_{\parallel})$ is obtained by multiplying the amplitude of the outgoing specular beam by $\frac{1}{2}(i)^2\theta^2(\vec{r},t)$

We now obtain rules for a diagrammatic scheme which enables us to obtain the form of the wave function for an arbitrary order in $\Delta(\vec{Q}_{\parallel})$, for the case where the slow frequency and spatial dependence of the scattering potential allow small-angle scatterings to provide the dominant contribution to the outgoing wave.

Consider that portion of the outgoing wave in Eq. (20) associated with scattering from the surface, accompanied by the emission of two surface phonons, the first with wave vector $\vec{Q}'_{\parallel}$ and the second with wave vector $\vec{Q}_{\parallel}$. In Fig. 1, we present an illustration of the character of the physical process responsible for each of the three terms in this portion of the wave function. In Fig. 1(a), the electron emits the two phonons on the outgoing portion of its trajectory. Omitting the δ functions which describe conservation of energy and wave vector, a glance at Eq. (20) shows that the processes of Fig. 1(a) make the contribution

$$R_0 \Delta(\vec{Q}_{\parallel})\Delta(\vec{Q}'_{\parallel})/\alpha_{Q_{\parallel}}(\alpha_{Q''_{\parallel}}\alpha_{Q'_{\parallel}}) \tag{24}$$

to the amplitude of the scattered wave function. From the structure of the perturbation series, this can be generalized to give a rule of computing the amplitude of the wave function of n phonons emitted by the electron after reflection from the surface. If the wave vectors of the phonons are $\vec{Q}_{\parallel}^{(1)}$, $\vec{Q}_{\parallel}^{(2)}, \ldots, \vec{Q}_{\parallel}^{(n)}$, with $\vec{Q}_{\parallel}^{(1)}$ emitted first and $\vec{Q}_{\parallel}^{(n)}$ emitted last, then the contribution to the wave function is found to be

$$\frac{\Delta(\vec{Q}_{\parallel}^{(n)})\cdots\Delta(\vec{Q}_{\parallel}^{(1)})}{\alpha_{Q_{\parallel}}^{(n)}(\alpha_{Q_{\parallel}}^{(n)}+\alpha_{Q_{\parallel}}^{(n-1)})\cdots(\alpha_{Q_{\parallel}}^{(n)}+\cdots+\alpha_{Q_{\parallel}}^{(1)})} . \tag{25}$$

From Figs. 1(b) and 1(c), along with the form of the wave function in Eq. (20), one sees that when a phonon is emitted on the *incoming* leg, a factor of $\alpha_{Q_{\parallel}}^*$ appears in the denominator rather than $\alpha_{Q_{\parallel}}$. The physical reason for this may be seen by considering the emission processes illustrated in Fig. 1. On the outgoing leg, emission of the particular surface phonon $\vec{Q}'_{\parallel}$ indicated in the figure *decrease* the normal component on the wave vector by an amount Δk_z, while emission of the same phonon on the incoming leg increases the normal component of the wave vector by the same amount. The matrix element of the scattering process is proportional to $(Q_{\parallel}+i\Delta k_z)^{-1}$, and changing the sign of Δk_z in the expression is equivalent to taking the complex conjugate.

By considering the remaining processes in Fig. 1, we arrive at the following set of rules for constructing the nth-order correction to the wave function. Before we write the rules down, recall that processes which involve more than one (or zero) direct reflection from the crystal surfaces must also contain at least one large-angle inelastic process, as we have pointed out previously.[7] As a consequence, such processes make a small contribution to the scattered wave, and we need only consider processes in which a single factor of the reflection coefficient is involved. With this in mind, the rules for constructing the wave function are

(a) Draw diagrams for all possible combinations of emissions and absorptions of phonons, along with a single reflection from the crystal surface.

(b) If the wave vectors of the phonons which enter the scattering process on the incoming portion of the trajectory have wave vectors $Q_{\parallel}^{(1)}, Q_{\parallel}^{(2)}, \ldots, Q_{\parallel}^{(n)}$, respectively, with $Q_{\parallel}^{(1)}$ the first in the sequence, multiply the wave function by the factor

$$[\beta_{Q_{\parallel}^{(1)}}(\beta_{Q_{\parallel}^{(1)}}+\beta_{Q_{\parallel}^{(2)}})\cdots(\beta_{Q_{\parallel}^{(1)}}+\cdots+\beta_{Q_{\parallel}^{(n)}})]^{-1},$$

where $\beta_{Q_{\parallel}^{(1)}} = \alpha_{Q_{\parallel}^{*(2)}}$ if the phonon is emitted, and

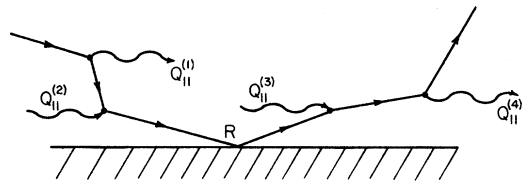

FIG. 2. A typical fourth-order contribution to the wave function.

$\beta_{Q_{\parallel}^{(1)}} = \alpha_{Q_{\parallel}^{(1)}}$ if the phonon is absorbed.

(c) If the phonons involved in scattering while the electron is on the outgoing portion of its trajectory have wave vectors $\vec{Q}_{\parallel}^{(1)}, \ldots, \vec{Q}_{\parallel}^{(n)}$, with $\vec{Q}_{\parallel}^{(n)}$ the last phonon, encountered by the electron, then multiply the wave function by $\beta_{Q_{\parallel}}^{*(n)}(\beta_{Q_{\parallel}}^{*(n)} + \beta_{Q_{\parallel}}^{*(n-1)}) \ldots (\beta_{Q_{\parallel}}^{*(n)} + \cdots + \beta_{Q_{\parallel}}^{*(1)})$, where $\beta_{Q_{\parallel}}$ is defined in rule (b).

(d) Add a factor of $i\Delta(\vec{Q}_{\parallel})$ for each phonon of wave vector $\vec{Q}_{\parallel}$ emitted, and a factor of $i\Delta^*(\vec{Q}_{\parallel})$ for each phonon absorbed.

(e) Include the δ functions which describe energy conservation, and conservation of wave vector parallel to the surface.

(f) Sum over all the $Q_{\parallel}$'s involved.

(g) Multiply by a factor of $(2\pi)^3 e^{ik_z z} R_0$, where R_0 is the specular reflection coefficient of the incident beam, and k_z is the wave vector normal to the surface of the scattered wave, calculated from the kinematics. For example, if the electron emits n phonons of wave vectors $\vec{Q}_{\parallel}^{(1)} \cdots \vec{Q}_{\parallel}^{(n)}$, and absorbs m phonons with wave vector $\vec{Q}_{\parallel}^{(n+1)} \cdots \vec{Q}_{\parallel}^{(n+m)}$, then for ω_s and $\vec{Q}_{\parallel}$ small, one may show that

$$k_z = k_{0z} + \frac{1}{V_\perp}[\vec{V}_{\parallel} \cdot (\vec{Q}_{\parallel}^{(1)} + \cdots + \vec{Q}_{\parallel}^{(n)} - \vec{Q}_{\parallel}^{(n+1)} - \cdots - \vec{Q}_{\parallel}^{(n+m)}) - (n-m)\omega_s]. \quad (25a)$$

Equation (25a) may also be written

$$k_z = k_{0z} + \sum_i \Delta k_z^{(i)},$$

where $\Delta k_z^{(i)}$ is the change in Δk_z associated with each elementary scattering process.

As an example of the diagrammatic rules, in Fig. 2 we show a fourth-order process. The contribution to the wave function from this process is

$$(2\pi)^3 R e^{ik_z z} \sum_{\vec{Q}_{\parallel}^{(1)} \cdots \vec{Q}_{\parallel}^{(4)}} \frac{(i)^4 \Delta(\vec{Q}_{\parallel}^{(1)}) \Delta^*(\vec{Q}_{\parallel}^{(2)}) \Delta^*(\vec{Q}_{\parallel}^{(3)}) \Delta(\vec{Q}_{\parallel}^{(4)}) \delta(\omega - E^{(0)}) \delta(\vec{k}_{\parallel} - \vec{Q}_{\parallel}^{(1)} + \vec{Q}_{\parallel}^{(2)} + \vec{Q}_{\parallel}^{(3)} - \vec{Q}_{\parallel}^{(4)} - \vec{k}_{\parallel}^{(I)})}{\alpha_{Q_{\parallel}}^{(4)}(\alpha_{Q_{\parallel}}^{(4)} + \alpha_{Q_{\parallel}}^{*(3)})\alpha_{Q_{\parallel}}^{*(1)}(\alpha_{Q_{\parallel}}^{*(1)} + \alpha_{Q_{\parallel}}^{(2)})}.$$

The general contribution to the wave-function nth order in the coupling parameter $\Delta(\vec{Q}_{\parallel})$ is difficult to write down compactly. We first examine a particular special contribution. Let the electron emit n phonons as it transverses its trajectory. There are $n+1$ contributions to the wave function from this process, given the n values of $\vec{Q}_{\parallel}$ involved, since the vertices can be arranged on the trajectory in $n+1$ ways relative to the point where the electron reflects from the surface. If we first imagine the diagram with all n phonons on the incoming portion of the trajectory, then we construct the remaining n diagrams by moving the lines one by one past the point where the electron reflects from the crystal surfaces. For each diagram in the sequence, the factors $\Delta(\vec{Q}_{\parallel}^{(1)}) \cdots \Delta(\vec{Q}_{\parallel}^{(n)})$ will be identical, as will be the δ function which conserves energy and wave vector. Each time we move a line past the specular reflection point, a factor in the denominator acquires a complex-conjugation sign. This process then gives a contribution to the wave function of the form (replacing $Q_{\parallel}^{(i)}$ by i for simplicity)

$$\psi_s^{(n1)} = (i)^n (2\pi)^3 e^{ik_z z} R_0 \sum_{1 \cdots n} \Delta_1 \Delta_2 \cdots \Delta_n \left(\frac{1}{\alpha_1^*(\alpha_1^* + \alpha_2^*)(\alpha_1^* + \cdots + \alpha_n^*)} + \frac{1}{\alpha_1^*(\alpha_1^* + \alpha_2^*) \cdots (\alpha_1^* + \cdots + \alpha_{n-1}^*)\alpha_n} \cdots + \frac{1}{(\alpha_1 + \cdots + \alpha_n) \cdots (\alpha_{n-1} + \alpha_n)\alpha_n} \right) \delta(\omega - E^{(0)} + n\omega_0) \delta(\vec{k}_{\parallel} - \vec{k}_{0\parallel} + \vec{Q}_{\parallel}^{(1)} + \cdots + \vec{Q}_{\parallel}^{(n)}). \quad (26)$$

Now form all $n!$ equivalent forms of $\psi_s^{(n1)}$ obtained from Eq. (26) by all possible permutations of the dummy indicies. Add all of these forms together, and divide by $n!$ to obtain a new expression for $\psi_s^{(n1)}$. The result assumes the form

$$\psi_s^{(n1)} = (i)^n (2\pi)^3 e^{ik_z z} \frac{R_0}{n!} \sum_{1 \cdots n} \Delta_1 \cdots \Delta_n \delta(\omega - E^{(0)} + n\omega_s) \delta(\vec{k}_{\parallel} - \vec{k}_{0\parallel} + \vec{Q}_{\parallel}^{(1)} + \cdots \vec{Q}_{\parallel}^{(n)}) \times \left(\frac{1}{\alpha_1^* \alpha_2^* \cdots \alpha_n^*} + \frac{1}{\alpha_1^* \alpha_2^* \cdots \alpha_{n-1}^* \alpha_n^*} + \cdots + \frac{1}{\alpha_1^* \alpha_2 \cdots \alpha_n} + \frac{1}{\alpha_1 \cdots \alpha_n} \right) \quad (27)$$

$$\equiv (i)^n \frac{(2\pi)^3 e^{ik_z z}}{n!} \sum_{1\cdots n} \Delta_1 \cdots \Delta_n \, \delta(\omega - E^{(0)} + n\omega_s) \, \delta(\vec{k}_\parallel - \vec{k}_\parallel + \vec{Q}_\parallel^{(1)} + \cdots \vec{Q}_\parallel^{(n)}) \left(\frac{\alpha_1 + \alpha_1^*}{\alpha_1 \alpha_1^*}\right) \cdots \left(\frac{\alpha_n + \alpha_n^*}{\alpha_n \alpha_n^*}\right) . \quad (28)$$

If the wave function in Eq. (28) is now transformed back to coordinate space, we obtain

$$\psi_s^{(n1)}(\vec{r}, t) = (i)^n \frac{R_0 e^{ik_z z}}{n!} \times \left(\sum_{\vec{Q}_\parallel} \frac{e^{-i\omega_s t} 2V_\perp Q_\parallel \Delta(\vec{Q}_\parallel) e^{i\vec{Q}\cdot\vec{r}}}{V_\perp^2 Q_\parallel^2 + (\omega_s - \vec{V}_\parallel \cdot \vec{Q}_\parallel)^2} \right)^n . \quad (29)$$

This is only one contribution to the scattered wave from processes in which n phonons are emitted by the electron when it scatters from the surface. For example, we can consider a process of order $n+2$, where one phonon out of the group is absorbed. This process will also lead to a contribution to the energy-loss peak at $n\omega_s$. It is easiest to confine our attention to terms of order n in $\Delta(\vec{Q}_\parallel)$, however. Thus, consider a diagram of order n, one phonon absorbed, and $(n-1)$ emitted.

The line associated with the absorbed phonon can be inserted at any one of the n vertices of a given diagram. The absorbed phonon has associated with it a factor of Δ^* rather than Δ. We note that the arguments of the δ functions which describe wave-vector conservation are invariant under interchange of any two *emitted* phonons. By considering all possible positions of the inserted absorbed phonon, a straightforward extension of the argument developed above may be employed to show that the process in which $(n-1)$ phonons are emitted and one absorbed leads to the contribution $\psi_s^{(n2)}$ given by

$$\psi_s^{(n2)} = \frac{(i)^n e^{ik_z z}}{n!} R_0 \sum_{1\cdots n} \delta[\omega + (n-2)\omega_s - E^{(0)}] \, \delta(\vec{k}_\parallel + \vec{Q}_\parallel^{(1)} - \vec{Q}_\parallel^{(2)} - \cdots \vec{Q}_\parallel^{(n)}) \times (\Delta_1^* \Delta_2 \cdots \Delta_n + \Delta_1 \Delta_2^* \Delta_3 \cdots \Delta_n + \cdots + \Delta_1 \Delta_2 \cdots \Delta_n^*) \left(\frac{2V_\perp Q_\parallel^{(1)}}{V_\perp^2 Q_\parallel^{(1)2} + (\omega_s - \vec{V}_\parallel \cdot \vec{Q}_\parallel^{(1)})^2}\right) \times \left(\frac{2V_\perp Q_\parallel^{(2)}}{V_\perp^2 Q_\parallel^{(2)2} + (\omega_s - \vec{V}_\parallel \cdot \vec{Q}_\parallel^{(2)})^2}\right) \cdots \left(\frac{2V_\perp Q_\parallel^{(n)}}{V_\perp^2 Q_\parallel^{(n)2} + (\omega_s - \vec{V}_\parallel \cdot Q_\parallel^{(n)})^2}\right) . \quad (30)$$

In fact, we may write down the outgoing portion of the wave function for the most general nth-order diagram, with l phonons emitted and m phonons absorbed, with $l+m=n$. The trend is quite clear from Eq. (30), and we shall quote the result, since the derivation is tedious, but straightforward after employing the arguments described above. We give the wave function in coordinate space, since it assumes its simplest form in that case. We find the wave function may be written in the form

$$\psi_s^{(n)}(\vec{r}, t) = (i)^n \frac{R_0 e^{i\vec{k}_0\cdot\vec{r}}}{n!} e^{-iE^{(0)}t} \times \left(\sum_{\vec{Q}_\parallel} \frac{2V_\perp Q_\parallel \Delta(\vec{Q}_\parallel)}{V_\perp^2 Q_\parallel^2 + (\omega_s - \vec{V}_\parallel \cdot \vec{Q}_\parallel)^2} e^{i\vec{Q}\cdot\vec{r}} e^{-i\omega_s t} + \text{c.c.} \right)^n ,$$

or in terms of the function $\theta(\vec{r}, t)$ introduced in Eq. (22), we have the remarkably simple result

$$\psi_s^{(n)}(\vec{r}, t) = R_0 e^{i(\vec{k}_0\cdot\vec{r} - E^{(0)}t)} \frac{i^n \theta^n(\vec{r}, t)}{n!} .$$

A closed expression is obtained by summing this result on n, from $n=0$ to ∞. One thus obtains the simple form

$$\psi_s(\vec{r}, t) = R_0 \exp[i\vec{k}_0\cdot\vec{r} - iE^{(0)}t - i\theta(\vec{r}, t)] . \quad (31)$$

This expression is the final result of the present section. Before we conclude the present section, we shall make a few remarks.

It should be stressed that the form in Eq. (31) gives only the outgoing portion of the wave function, far from the crystal. It is only valid provided the electron is sufficiently far from the crystal that is propagates as if in free space, free of any perturbation by the crystal. The wave vector $\vec{k}_0$ is that of the outgoing specular beam, and R_0 is the specular reflection coefficient, from the rigid crystal.

Notice the only assumption beyond those contained in the model that we have made in order to derive Eq. (31) is that the potential set up by the lattice motion varies in time slowly compared to $E^{(0)}/\hbar$, and slowly in space on the scale of the de Broglie wavelength of the electron. The first assumption is always well satisfied for electrons with energies in the electron-volt range, and the second assumption will be valid for those electrons which emerge near the specular direction. So long as these assumptions are satisfied, the

wave function is valid even when the electron-phonon coupling is very large.

III. GENERAL DISCUSSION: DERIVATION OF THE INELASTIC-SCATTERING CROSS SECTION FOR INTERACTION WITH THERMAL PHONONS

We begin with a discussion of the physical picture one obtains of the scattering process from our approach. We consider the scattering of an electron by a contrived potential which produces a wave function very similar to that in Eq. (31). This will give one a feeling for the nature of the interaction of the electron with the surface optical phonon. Then we shall proceed to derive the form of the cross section for inelastic scattering of the electron by thermally excited surface optical modes. We see at this point that our theory agrees in this case with the earlier work of Lucas and Sunjic although we feel our discussion is more general than theirs, for reasons described in the Introduction.

Consider an electron moving through a potential $V(\vec{x}, t)$ which varies slowly in time and space. The wave function may be written, quite generally, [10]

$$\psi(\vec{x}, t) = A(\vec{x}, t)\, e^{i\varphi(\vec{x}, t)},$$

where the functions A and θ are real and satisfy

$$\frac{\partial \varphi}{\partial t} + \frac{(\nabla\varphi)^2}{2m} - \frac{1}{2m}\frac{\nabla^2 A}{A} = -V(\vec{x}, t)\ , \tag{32a}$$

$$m\frac{\partial A}{\partial t} + \nabla A\cdot\nabla\varphi + \frac{A}{2}\nabla^2\varphi = 0\ . \tag{32b}$$

If V varies slowly in space and time, then one may argue that the third term on the left-hand side in Eq. (32a) may be ignored, since it is second order in the ratio of the de Broglie wavelength of the particle to the length that characterizes the spatial variation of $V(\vec{x}, t)$. Thus, we may take A to be constant, and φ satisfies

$$\frac{\partial \varphi}{\partial t} + \frac{1}{2m}(\nabla\varphi)^2 = -V(\vec{x}, t)\ . \tag{33}$$

Now write $\varphi = \vec{k}_0\cdot\vec{r} - E^{(0)}t + \theta(\vec{r}, t)$, where $\theta(\vec{r}, t)$ varies slowly in space and time. To first order in the space and time dependence of θ, Eq. (33) becomes

$$\frac{\partial\theta}{\partial t} + \vec{V}_0\cdot\nabla\theta = -V(\vec{x}, t)\ , \tag{33a}$$

where $\vec{V}_0 = \vec{k}_0/m$.

Now for $V(\vec{x}, t)$ we take the form

$$V(\vec{x}, t) = \Delta e^{-Q_{\parallel}|z|}\, e^{i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel}}\, e^{-i\omega_s t} + \text{c.c.}$$

The problem we consider is that of the transmission of an electron through a potential similar to that set up by excitation of a surface optical phonon. In this discussion, we omit the sharp step represented by $V_0(\vec{x})$ in the discussion of Sec. II. The present method does not enable us to discuss the influence of the rapidly varying step potential.

Now we look for solutions of Eq. (33). Let

$$\theta(\vec{x}, t) = e^{i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel} - i\omega_s t}\begin{cases}\theta_+ e^{-Q_{\parallel}z}, & z>0\\ \theta_- e^{+Q_{\parallel}z}, & z<0\ .\end{cases} \tag{34}$$

From Eq. (33), one finds

$$\theta_{\pm} = \frac{\Delta}{i(\omega_s - \vec{V}_{\parallel}\cdot\vec{Q}_{\parallel}) \pm V_{\perp}Q_{\parallel}}\ . \tag{35}$$

There is also a solution of the homogeneous part of Eq. (33a):

$$\theta(\vec{x}, t) = C\exp[i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel} - i\omega_s t + i\Delta k_z z]\ ,$$

where

$$\Delta k_z = \frac{1}{V_{\perp}}(\omega_s - \vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})\ .$$

If we now require that $\theta(x, t)$ be continuous at $z = 0$, and also that $\theta \to 0$ as $z \to -\infty$, then in the region $z > 0$, $\theta(\vec{x}, t)$ becomes

$$\theta(\vec{x}, t) = \Delta e^{i[\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel} - \omega_s t]}\left(\frac{e^{-Q_{\parallel}z}}{i(\omega_s - \vec{V}_{\parallel}\cdot\vec{Q}_{\parallel}) + V_{\perp}Q_{\parallel}} - \frac{2V_{\perp}Q_{\parallel}e^{i\Delta k_z z}}{(\omega_s - \vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2 + V_{\perp}^2Q_{\parallel}^2}\right) + \text{c.c.} \tag{36}$$

Then, as $z \to \infty$, the wave function becomes

$$\psi(\vec{x}, t) = \exp\left(i\vec{k}_0\cdot\vec{x} - iE^{(0)}t - \frac{2iV_{\perp}Q_{\parallel}\Delta}{(\omega_s - \vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2 + V_{\perp}^2Q_{\parallel}^2}e^{i(\vec{Q}\cdot\vec{x} - \omega_s t)} + \text{c.c.}\right), \tag{37}$$

where $\vec{Q} = \vec{Q}_{\parallel} + \hat{z}\Delta k_z$.

The wave function in Eq. (37) is very similar to the form obtained in Sec. II, for the case where the electron scatters from the crystal surface. We may now obtain a simple physical picture of how the wave function in Eq. (31) of Sec. II is produced. As the electron moves in towards the crystal, it encounters the potential set up by the surface optical mode. This potential varies slowly in space and time, and the phase of the electron's wave function is modulated in an adiabatic fashion. If the electron is at the point $(\vec{x}, t)$ on the outgoing portion of its trajectory, and is also far from the crystal surface, then $\theta(\vec{x}, t)$ measures the amount by which the phase has been modulated by the potential.

We next derive the form of the energy-loss cross section, from Eq. (31). For this purpose, we write for the phase angle $\theta(\vec{r}, t)$ of Eq. (31),

$$\theta(\vec{r}, t) = \gamma(\vec{r})e^{i\omega_s t} + \gamma^*(\vec{r})e^{i\omega_s t}, \tag{38a}$$

where

$$\gamma(\vec{r}) = \sum_{\vec{Q}_\parallel} \gamma(\vec{Q}_\parallel) e^{i\vec{Q}\cdot\vec{r}} , \tag{38b}$$

with

$$\gamma(\vec{Q}_\parallel) = \frac{2V_\perp Q_\parallel \Delta(\vec{Q}_\parallel)}{V_\perp^2 Q_\parallel^2 + (\omega_s - \vec{V}_\parallel \cdot \vec{Q}_\parallel)^2} . \tag{38c}$$

In our previous work, we examined the angular distribution of electrons scattered by one-phonon processes. Here we use a method which gives the intensity of the outgoing beam associated with the n phonon loss of gain process, but we will not study the details of the angular distribution.

We begin by noting that we may expand the function $e^{i\theta(\vec{r},t)}$ in a Fourier series in time as follows:

$$e^{i\theta(\vec{r},t)} = \sum_{n>0} A_n e^{in\omega_s t} + \sum_{n>0} A_n^* e^{-in\omega_s t} .$$

The intensity I_n of the outgoing beam associated with the gain or loss of n phonons is just given by $|R_0|^2|A_n|^2$. [We see the energy-gain and energy-loss cross sections are equal. This is a consequence of our treatment of $\Delta(\vec{Q}_\parallel)$ as a classical dynamical variable, and not a true boson operator. In the classical limit, valid when $kT \gg \hbar\omega_s$, the energy-loss and energy-gain cross sections become equal.]

Now we have

$$A_n = \frac{\omega_s}{2\pi}\int_0^{2\pi/\omega_s} dt\, e^{in\omega_s t} \exp(i\gamma e^{i\omega_s t} + i\gamma^* e^{-i\omega_s t}) \tag{39}$$

and if we change variables by letting $\tau = \omega_s t$, then form the expression for $|A_n|^2$, a short calculation gives

$$|A_n|^2 = \frac{1}{(2\pi)^2}\int_0^{2\pi} d\tau_1 \int_0^{2\pi} d\tau_2\, e^{in(\tau_1-\tau_2)} \times e^{i[\gamma\beta(\tau_1,\tau_2)+\gamma^*\beta^*(\tau_1,\tau_2)]} ,$$

where

$$\beta(\tau_1, \tau_2) = e^{i\tau_1} - e^{i\tau_2} .$$

As we stated in Sec. II, the parameter $\Delta(\vec{Q}_\parallel)$ is proportional to the amplitude of the surface phonon. If we call $u(Q_\parallel, t)$ the normal coordinate of mode $Q_\parallel$, then

$$u(Q_\parallel, t) = u_+(Q_\parallel) e^{i\omega_s t} + u_-(Q_\parallel) e^{-i\omega_s t} ,$$

and $\Delta(\vec{Q}_\parallel)$ is proportional to the amplitude $u_+(Q_\parallel)$ of the positive frequency part, while $\Delta^*(\vec{Q}_\parallel)$ is proportional to $u_-(Q_\parallel)$. Then to calculate the amplitude of the scattered wave, we must perform a statistical average over the amplitudes of the normal modes. Denote the statistically averaged intensity by $\langle|A_n|^2\rangle$. Then

$$\langle|A_n|^2\rangle = \frac{1}{(2\pi)^2}\int_0^{2\pi} d\tau_1 \int_0^{2\pi} d\tau_2 e^{in(\tau_1-\tau_2)} \langle e^{i\gamma\beta + i\gamma^*\beta^*}\rangle . \tag{40}$$

In our model, the average is to be taken by the methods of classical statistical mechanics. At this point, we could invoke the correspondence principle, and proceed to obtain the general result. However, we have found the classical calculation instructive, so we present it first, and quote the general result later. Note that β is a parameter independent of both $\vec{Q}_\parallel$ and the phonon amplitude. Now from Eq. (38b),

$$\gamma(\vec{r}) = \sum_{\vec{Q}_\parallel} \gamma(\vec{Q}_\parallel) e^{i\vec{Q}\cdot\vec{r}} .$$

Each normal mode is independent, in the harmonic approximation, and

$$\langle e^{i\gamma\beta} e^{i\gamma^*\beta^*}\rangle = \prod_{\vec{Q}_\parallel} \langle \exp[i\beta\gamma(\vec{Q}_\parallel) e^{i\vec{Q}\cdot\vec{r}}] \times \exp[i\beta^*\gamma^*(\vec{Q}_\parallel) e^{-i\vec{Q}\cdot\vec{r}}]\rangle .$$

Consider the averaging process for a particular value of $\vec{Q}_\parallel$. For compactness, we omit the index $\vec{Q}_\parallel$ from the quantities that follow. If u_+ and u_- are the positive and negative frequency components of the displacement field, respectively, then

$$\gamma = \lambda u_+ , \quad \gamma^* = \lambda^* u_- ,$$

where the form of the proportionality coefficients follow from Eq. (38).

Now

$$\langle e^{i\beta\lambda u_+} e^{i\beta^*\lambda^* u_-}\rangle = \sum_{n=0} \frac{(i)^n}{n!} \langle(\lambda\beta u_+ + \lambda^*\beta^* u_-)^n\rangle ,$$

where

$$\langle(\lambda\beta u_+ + \lambda^*\beta^* u_-)^n\rangle = \sum_{m=0}^{n} \frac{n!}{m!(n-m)!} \times (\lambda\beta)^{n-m} (\lambda^*\beta^*)^m \langle u_+^{n-m} u_-^m\rangle .$$

Thus, our task is to compute $\langle u_+^{n-m} u_-^m\rangle$. Instead of averaging over u_+ and u_-, we write

$$u_+ = ue^{i\varphi} , \quad u_- = ue^{-i\varphi} ,$$

and average over u and φ separately. Now the average over a function of u is taken according to the following prescription:

$$\langle f(u_+, u_-)\rangle = \int d^2u\, e^{-E(u)/kT} f(u_+, u_-) / \int d^2u\, e^{-E(u)/kT}$$

$$= \int_0^\infty du\, u\, e^{-E(u)/kT} \int_0^{2\pi} d\varphi f(u_+, u_-) / \int_0^\infty du\, u\, e^{-E(u)/kT} \int_0^{2\pi} d\varphi ,$$

where $E(u)$ is the energy of the oscillator when it has amplitude u. Of course, $E(u)$ is proportional to u^2 for a harmonic oscillator. With this prescription, one may readily demonstrate that

$$\langle u_+^{n-m} u_-^m\rangle = \begin{cases} 0 & \text{if } n \text{ is odd} \\ n!\ \langle u^2\rangle^n\ \delta_{n,m} & \text{if } n \text{ is even.} \end{cases} \tag{41}$$

In Eq. (41), $\langle u^2\rangle$ is the mean-square displacement of the oscillator.

With this result, it is a short exercise to demon-

strate that

$$\langle \exp[i\beta\gamma(\vec{Q}_{\parallel})e^{i\vec{Q}\cdot\vec{r}}]\exp[i\beta^*\gamma^*(\vec{Q}_{\parallel})e^{-i\vec{Q}\cdot\vec{r}}]\rangle = e^{-|\beta|^2\langle|\gamma(\vec{Q}_{\parallel})|^2\rangle} .$$

The quantity $|\gamma(\vec{Q}_{\parallel})|^2$ is independent of $\vec{r}$, so we write

$$\langle e^{i\gamma(\vec{r})\beta}e^{i\gamma^*(\vec{r})\beta}\rangle = \exp[-|\beta|^2\sum_{\vec{Q}_{\parallel}}\langle|\gamma(\vec{Q}_{\parallel})|^2\rangle] ,$$

$$\langle|\gamma(\vec{Q}_{\parallel})|^2\rangle = \frac{4V_{\perp}^2Q_{\parallel}^2\langle|\Delta(\vec{Q}_{\parallel})|^2\rangle}{[V_{\perp}^2Q_{\parallel}^2+(\omega_s-\vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2]^2} .$$

We now return to Eq. (40), and recall the definition of the parameter β. We then find

$$\langle|A_n|^2\rangle = \exp[-2\sum_{\vec{Q}_{\parallel}}\langle|\gamma(\vec{Q}_{\parallel})|^2\rangle]\frac{1}{2\pi^2}\int_0^{2\pi}d\tau_1\int_0^{2\pi}d\tau_2\exp[in(\tau_1-\tau_2)]\exp[+2\sum_{\vec{Q}_{\parallel}}\langle|\gamma(\vec{Q}_{\parallel})|^2\rangle\cos(\tau_1-\tau_2)]$$

$$= \exp[-2\sum_{\vec{Q}_{\parallel}}\langle|\gamma(\vec{Q}_{\parallel})|^2\rangle]\int_0^{2\pi}\frac{d\theta e^{in\theta}}{2\pi}\exp[2\sum_{\vec{Q}_{\parallel}}\langle|\gamma(\vec{Q}_{\parallel})|^2\rangle\cos(\theta)]$$

or, finally

$$\langle|A_n|^2\rangle = \exp[-2\sum_{\vec{Q}_{\parallel}}\langle|\gamma(\vec{Q}_{\parallel})|^2\rangle]I_n[2\sum_{Q_{\parallel}}\langle|\gamma(\vec{Q}_{\parallel})|^2\rangle] . \quad (42)$$

In Eq. (42) $I_n(x)$ is the modified Bessel function of order x.[11]

Equation (42) is the final result of our classical theory. The intensity of the beam associated with the gain or loss of n phonons is just $|R_0|^2\langle|A_n|^2\rangle$, in our model,

$$I_n = |R_0|^2\langle|A_n|^2\rangle .$$

We see quite explicitly that the intensity of the inelastically scattered electrons is proportional to the specular reflection coefficient. This result seems amply confirmed by Ibach's experiments on ZnO.[5]

The result in Eq. (41) is valid only where the classical limit applies. This result for the ratio (I_n/I_0) of the cross section for the loss or gain of n phonons to the specular intensity is in agreement with the high-temperature form of the Lucas-Sunjic theory[12] in the region $kT \gg \hbar\omega_s$.

We conclude this section by showing how the correspondence principle may be used to extend our treatment to all temperatures. To do this, in the expression for A_n [Eq. (39)] one replaces the classical variables γ and γ^* by the appropriate boson annihilation and creation operators that annihilate and create surface phonons, respectively. Then, in performing the statistical average, we average $|A_n|^2$ over the appropriate quantum ensemble.

In our preceding argument, we have used the fact that (omitting the recurrent factor of $\vec{Q}_{\parallel}$)

$$\gamma = \lambda u_+(\vec{Q}_{\parallel}), \quad \gamma^* = \lambda^* u_-(\vec{Q}_{\parallel}) .$$

But $u_+(\vec{Q}_{\parallel})$ and $u_-(\vec{Q}_{\parallel})$ are proportional to $a^\dagger(\vec{Q}_{\parallel})$ and $a(\vec{Q}_{\parallel})$, respectively. Thus

$$\gamma(\vec{Q}_{\parallel}, r) = g(\vec{Q}_{\parallel}, \vec{r})a^\dagger(\vec{Q}_{\parallel})$$

and

$$\gamma^*(\vec{Q}_{\parallel}, \vec{r}) = g^*(\vec{Q}_{\parallel}\vec{r})a(\vec{Q}_{\parallel}) .$$

The function $g(\vec{Q}_{\parallel}, \vec{r})$ for the case of ZnO and Si are easily obtained from our previous paper, where the parameters $\Delta(\vec{Q}_{\parallel})$ and $\Delta^*(\vec{Q}_{\parallel})$ are related to $a(\vec{Q}_{\parallel})$ and $a^\dagger(\vec{Q}_{\parallel})$. Then, for $\langle|A_n|^2\rangle$ we obtain

$$\langle|A_n|^2\rangle = \frac{\omega_s^2}{4\pi^2}\int_0^{2\pi/\omega_s}dt\int_0^{2\pi/\omega_s}dt\, e^{in\omega_s(t_1-t_2)} \times\prod_{\vec{Q}_{\parallel}}\langle\exp[i\Gamma(\vec{Q}_{\parallel}, t_1)]\exp[-i\Gamma(\vec{Q}_{\parallel}, t_2)]\rangle ,$$

where

$$\Gamma(\vec{Q}_{\parallel}, t) = e^{i\omega_s t}[g(\vec{Q}_{\parallel}\vec{r})a^\dagger(\vec{Q}_{\parallel}) + g^*(\vec{Q}_{\parallel}, \vec{r})a(\vec{Q}_{\parallel})].$$

The average is over the appropriate quantum statistical ensemble. One may easily show that

$$\langle|A_n|^2\rangle = \frac{\omega_s}{2\pi}\int_0^{2\pi/\omega_s}dt e^{in\omega_s t}\prod_{\vec{Q}_{\parallel}}\langle e^{i\Gamma(\vec{Q}_{\parallel},t)}e^{i\Gamma(\vec{Q}_{\parallel},0)}\rangle .$$

The statistical average is readily carried out by the use of standard methods. For our particular problem, this has been discussed in detail by Lucas and Sunjic.[12] One has

$$\langle e^{i\Gamma(\vec{Q}_{\parallel},t)}e^{-i\Gamma(\vec{Q}_{\parallel},0)}\rangle = \exp[-|g(\vec{Q}_{\parallel})|^2(1+2\bar{n})] \times\exp[|g(\vec{Q}_{\parallel})|^2(1+\bar{n})e^{i\omega_s t}+|g(\vec{Q}_{\parallel})|^2\bar{n}e^{i\omega_s t}] ,$$

where $|g(\vec{Q}_{\parallel}, \vec{r})|^2$ is independent of $\vec{r}$, and

$$\bar{n} = (e^{\hbar\omega_s/kT}-1)^{-1}$$

is the number of thermally excited surface phonons present at temperature T. Then

$$\langle|A_n|^2\rangle = \frac{\omega_s}{2\pi}\exp[-\sum_{\vec{Q}_{\parallel}}|g(\vec{Q}_{\parallel})|^2(1+2\bar{n})]\int_0^{2\pi/\omega_s}dt \times e^{in\omega_s t}\exp\{\sum_{\vec{Q}_{\parallel}}|g(\vec{Q}_{\parallel})|^2[(1+\bar{n})e^{i\omega_s t}+\bar{n}e^{-i\omega_s t}]\} . \quad (43)$$

Equation (43) is identical to the classical result

displayed in integral form just before Eq (42), in the limit $\bar{n} \gg 1$ appropriate to the classical regime. Equation (43) is also identical to the finite-temperature form of the Lucas-Sunjic theory,[12] provided we identify our parameter $\langle |A_n|^2 \rangle$, related to the magnitude of the intensity I_n of the beam associated with the energy loss $n\omega_s$ by the relation $I_n = |R_0|^2 \langle |A_n|^2 \rangle$, with their parameter P_n.

The expression in Eq. (43) may be written in a closed analytic form, valid for all temperatures. We quote the result, since we have not seen this form displayed before. Let

$$\Gamma = \sum_{\vec{Q}_\parallel} |g(\vec{Q}_\parallel)|^2 , \tag{44a}$$

or

$$\Gamma \equiv \tanh\left(\frac{\hbar\omega_s}{2kT}\right) \sum_{\vec{Q}_\parallel} \frac{4V_\perp^2 Q_\parallel^2 \langle |\Delta(\vec{Q}_\parallel)|^2 \rangle}{[V_\perp^2 Q_\parallel^2 + (\omega_s - \vec{V}_\parallel \cdot \vec{Q}_\parallel)^2]^2} . \tag{44b}$$

Equation (44b) follows upon relating the average $\langle |\Delta(\vec{Q}_\parallel)|^2 \rangle$ (taken over a quantum statistical ensemble) back to $|g(\vec{Q}_\parallel)|^2$. The average $\langle |\Delta(\vec{Q}_\parallel)|^2 \rangle$ is proportional to $\coth(\hbar\omega_s/2k_BT)$ so the right-hand side of Eq. (44b) is in fact temperature independent.

Then Eq. (43) becomes

$$\langle |A_n|^2 \rangle = (1+\bar{n})^n \frac{I_n\{2\Gamma[\bar{n}(1+\bar{n})]^{1/2}\}}{[\bar{n}(1+\bar{n})]^{n/2}} e^{-\Gamma(1+2\bar{n})} . \tag{45}$$

If $\bar{n} \gg 1$ (the classical region), Eq. (45) reduces to the result in Eq. (42), provided the correspondence between $|g(\vec{Q}_\parallel)|^2$ and $|f(\vec{Q}_\parallel)|^2$ is noted.

At low temperatures, $\bar{n} \ll 1$. Then since $I_n(2x) \approx x^n/n!$ for $x \ll 1$, one finds

$$\langle |A_n|^2 \rangle = \Gamma^n/n!\, e^{-\Gamma} . \tag{46}$$

This is just the Poisson distribution function that has been employed to interpret the data on ZnO taken at room temperature by Ibach.

Equation (45) gives the cross section associated with the emission of n phonons. The cross section associated with the absorption of n thermal phonons is given by $\langle |A_{-n}|^2 \rangle$. One finds that

$$\langle |A_{-n}|^2 \rangle = (\bar{n})^n \frac{I_n\{2\Gamma[\bar{n}(1+\bar{n})]^{1/2}\}}{[\bar{n}(1+\bar{n})]^{n/2}} e^{-\Gamma(1+2\bar{n})} . \tag{46a}$$

The energy-gain and energy-loss cross sections become equal when $\bar{n} \gg 1$, and $\langle |A_{-n}|^2 \rangle \to 0$ as $\bar{n} \to 0$.

A number of properties of the cross section have been discussed by Lucas and Sunjic.[12] For completeness, we recall these results.

The intensities $\langle |A_n|^2 \rangle$ for general temperatures satisfy a sum rule

$$\sum_n \langle |A_n|^2 \rangle = 1. \tag{47}$$

Thus, as the electron-phonon coupling strength is increased, the intensity I_0 of the specular beam falls, and the fraction of the electrons in the inelastic beams increases in such a manner that the *total* fraction of electrons reflected is just $|R_0|^2$, the specular reflection coefficient in the absence of electron-phonon coupling.

In the presence of electron-phonon coupling, the coefficient for specular reflection is reduced, and becomes

$$I_0 = |R_0|^2 I_0\{2\Gamma[\bar{n}(1+\bar{n})]^{1/2}\} e^{-\Gamma(1+2\bar{n})} . \tag{48}$$

From the discussion of the second-order corrections to the wave function in Sec. II, we see that the elastically scattered electrons do not emerge only in the specular direction, but are distributed over angular range centered on the specular direction. While we have not explicitly studied the angular distribution of the elastics, it is clear from the nature of the second-order corrections to the wave function and our previous discussion[7] of the angular distribution of the electrons scattered by one-phonon processes that the elastically scattered electrons are spread over the angle $\varphi_E = \hbar\omega_s/2E^{(0)}$, the same angle that describes the angular width of the inelastic beam.[7]

Lucas and Sunjic[12] also point our that the mean number $\langle n \rangle$ of phonons excited by the electron is independent of temperature, and is given simply by

$$\langle n \rangle = \Gamma , \tag{49}$$

where Γ is the parameter that enters Eq. (45), and defined in Eq. (44).

IV. INELASTIC SCATTERING OF A LOW-ENERGY ELECTRON BY A COHERENTLY GENERATED SURFACE OPTICAL WAVE

In Sec. III, we discussed the form of the scattering cross section for the case where the electron scatters from thermally excited surface phonons. In this section, we compare the results of Sec. III with the cross section for scattering of an electron beam from a surface optical phonon generated by an external source. For the case of Fuchs-Kliewer modes on the surface of an ionic crystal, at least, in principle, such a wave may be generated by placing a periodic grating structure on the surface, and irradiating the structure with infrared radiation. The presence of surface roughness will also lead to coupling between an external source and the surface wave.

Suppose that a coherent surface wave vector with wave vector $\vec{Q}_\parallel$ is generated on the surface. Our derivation of Sec. II, which treats the potential set up by the wave in a classical manner, may be used to obtain the wave function of the outgoing electron. In fact, the wave function has just the form exhibited in Eq. (31):

$$\psi_s(\vec{r}, t) = R_0 \exp[i\vec{k}_0 \cdot \vec{r} - iE^{(0)}t - i\theta(\vec{r}, t)] , \tag{50}$$

where in the expression for $\theta(\vec{r}, t)$ we keep only the contribution from the single Fourier component

$\vec{Q}_{\parallel}$ associated with the driven wave. From Eq. (22), we take $\theta(\vec{r}, t)$ to have the form

$$\theta(\vec{r}, t) = \frac{2V_{\perp}Q_{\parallel}}{V_{\perp}^2 Q_{\parallel}^2 + (\omega_s - \vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2} \times[\Delta(\vec{Q}_{\parallel})e^{i\vec{Q}\cdot\vec{r}}e^{-i\omega_s t} + \text{c.c.}] \quad (51a)$$

$$= \gamma(\vec{Q}_{\parallel})e^{i\vec{Q}\cdot\vec{r}}e^{-i\omega_s t} + \gamma^*(\vec{Q}_{\parallel})e^{i\vec{Q}\cdot\vec{r}}e^{+i\omega_s t}, \quad (51b)$$

where, as in Sec. III,

$$\gamma(\vec{Q}_{\parallel}) = \frac{2V_{\perp}Q_{\parallel}\Delta(\vec{Q}_{\parallel})}{V_{\perp}^2 Q_{\parallel}^2 + (\omega_s - \vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2}\,.$$

The physical content of the wave function in Eq. (50) may be appreciated by expanding the factor of $e^{-i\theta(\vec{r},t)}$ in a power series in $\gamma(\vec{Q}_{\parallel})$. One has

$$\gamma_s(\vec{r}, t) = R_0\exp[i\vec{k}_0\cdot\vec{r} - iE^{(0)}t] + R_0\sum_{n=1}^{\infty}\frac{\gamma(\vec{Q}_{\parallel})^n}{n!}\exp[i(\vec{k}_0+n\vec{Q})\cdot\vec{r} - i(E^{(0)}+n\omega_s)t] + R_0\sum_{n=1}^{\infty}\frac{\gamma^*(\vec{Q}_{\parallel})^n}{n!}\exp[(\vec{k}_0-n\vec{Q})\cdot\vec{r} - i(E^{(0)}-n\omega_s)t]. \quad (52)$$

The electron is thus Bragg reflected from the periodic disturbance on the surface, and the scattered wave displays an array of discreet Bragg peaks at the positions $\vec{k}_s = \vec{k}_0 \pm n\vec{Q}$. Recall that

$$\vec{Q} = \vec{Q}_{\parallel} + \frac{1}{V_{\perp}}(\vec{V}_{\parallel}\cdot\vec{Q}_{\parallel} - \omega_s)\hat{z}\,.$$

The Bragg scattering is inelastic, in the sense that the nth-order beam emerges with its frequency shifted up or down by the amount $n\omega_s$. The electron is, in effect, Bragg reflected from a moving grating, and the frequency shift is a Doppler shift.

The form in Eq. (52) allows one to calculate the intensity of the nth-order Bragg beam. This must be done with some care, since the various beams interfere coherently, i.e., the intensity of the nth-order beam is not simply $|R_0|^2|\gamma(\vec{Q}_{\parallel})|^{2n}/(n!)^2$, as one would get by directly squaring the coefficients in Eq. (52) of the terms proportional to $e^{iE^{(0)}\pm n\omega_s t}$.

The intensity of the nth-order beam is given by the quantity $|R_0|^2|A_n|^2$, where $|A_n|^2$ is the amplitude discussed in Sec. III. To calculate $|A_n|^2$, we may use Eq. (39) directly for the quantity A_n:

$$A_n = \frac{\omega_s}{2\pi}\int_0^{2\pi/\omega_s} dt\, e^{in\omega_s t} \times\exp\{i[\gamma(\vec{Q}_{\parallel})e^{i\omega_s t} + \gamma^*(\vec{Q}_{\parallel})e^{-i\omega_s t}]\}, \quad (53)$$

where $\gamma(\vec{Q}_{\parallel})$ is to be treated as a classical amplitude. The statistical averaging procedure that entered into the discussion of this section is omitted here, since $\gamma(\vec{Q}_{\parallel})$ is a classical variable, with well-defined amplitude and phase. It is straightforward to show that

$$A_n = (i)^n J_n[2|\gamma(\vec{Q}_{\parallel})|]\,.$$

The intensity of the nth Bragg beam is then

$$I_n = I_{-n} = |R_0|^2|J_n[2|\gamma(\vec{Q}_{\parallel})|]|^2\,. \quad (54)$$

Notice that the intensity of the wave shifted in frequency away from $E^{(0)}/\hbar$ by the frequency $n\omega_s$ is quite different for the two cases considered here—the case where the electron scatters from the coherently excited wave, and from thermal phonons. The physical origin of the difference is clear. As the electron approaches the crystal for the case in which a surface wave has been generated in a coherent fashion, as it multiply scatters from the potential associated with the wave (to use a language suggested by the discussion in Sec. II), it carries with it information about the well-defined phase present in the wave. In a multiple-scattering process associated with a given order, the various possible scattering paths contribute coherently to the amplitude of the outgoing wave. On the other hand, when the electron undergoes a sequence of scatterings produced by thermally excited surface waves, crudely speaking the electron sees a different phonon at each scattering event, and the phase coherence between the various scatterings is not present. In our classical treatment, this feature of the multiple-scattering theory enters the mathematics in the statistical averaging procedure which precedes Eq. (41). The phase coherence between successive scatterings in a given order is wiped out when the phase variable φ is averaged over.

When the electron scatters from the coherently driven wave, the *total* reflected intensity given by

$$I_{\text{tot}} = \sum_{n=-\infty}^{+\infty} I_n$$

is just equal to the intensity $|R_0|^2$ associated with the rigid crystal. This is ensured by the well-known Bessel-function sum rule[13]

$$|J_0(x)|^2 + 2\sum_1^{\infty}|J_n(x)|^2 = 1\,.$$

When the wave is excited, the intensity of the specular beam is reduced to the value

$$I_0 = |R_0|^2|J_0[2\gamma(\vec{Q}_{\parallel})]|^2\,,$$

and the remaining portion is distributed over the inelastically scattered beams. As we saw in Sec. III, the same sum rule obtains for the scattering from thermal phonons.

We conclude with two final comments. The results displayed in this section depend explicitly on the wave nature of the electron, and cannot be produced by the semiclassical theory of Lucas and Sunjic, which treats the electron as a point, classical particle. Finally, there is a close formal analogy between the theory of low-energy electron scattering from a coherently generated surface-optical-phonon wave, and the theory of microwave-induced steps in Josephson junctions.[14]

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Dielectric Susceptibility and Infrared Absorption in Cubic Crystals Containing Substitutional Impurities

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Using thermodynamic double-time Green's-function methods and Kubo formalism, theoretical expressions are obtained for the dielectric susceptibility and infrared-absorption coefficient of a Bravais crystal containing randomly distributed substitutional impurities. Mass changes as well as force-constant changes between the impurity atoms and the host-lattice atoms are explicitly included. It is found that these expressions contain some nondiagonal contributions in addition to the usual diagonal contributions. For phonons of small half-width, the linear absorption coefficient is proportional to the half-width, which in turn varies as the square of the sum of the mass and force-constant changes. Contributions due to localized modes are also obtained.

I. INTRODUCTION

It is well known that the introduction of defects into crystals greatly modifies their optical and dynamical properties.[1,2] Such modifications are largest in the vicinity of the defects. Comprehensive literature[3] is available discussing the dynamics of crystal lattices with defects, both theoretically and experimentally. The Mössbauer effect from the impurity has been used to investigate the mean-square amplitude and energy of the defect atom.[4] However, these properties are not very sensitive to details of the spectrum because they involve averages over all the perturbed modes. Another method, based on the measurement of optical absorption by one-phonon processes, appears to present a much simpler method to study the motion of defects because of the direct link between the absorption line shape and the structure of the phonon spectrum of the impure crystal. Such impurity absorption is known to occur in covalent crystals such as diamond where, by symmetry,