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PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

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

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(Received 22 October 1971)

The purpose of this paper is to present a quantum-mechanical theory of the inelastic scattering of slow electrons by long-wavelength surface optical phonons for simple models of an ionic crystal and for a nonionic crystal such as silicon. It is argued that a quantum-mechanical approach is necessary for this problem. However, the expression we obtain for the one-phonon cross section is found to be identical to the one that follows from the earlier classical theory of Lucas and co-workers, provided one replaces their parameter P_0 by the quantum-mechanical reflection coefficient for specular reflection. The angular distribution of the scattered electrons and the energy dependence of the one-phonon cross section are discussed for the case of ZnO and silicon, where the surface optical modes have a very different character. For the surface mode in silicon, we define a dipole-moment effective charge, which is nonzero by virtue of the absence of inversion symmetry in the surface region. A quantitative estimate of the magnitude of this parameter is extracted from the data of Ibach.

I. INTRODUCTION

The effect of a surface on the phonon spectrum of crystals and on the magnetic properties of crystals has been the subject of a considerable theoretical effort. In many instances, the theory has reached a high level of sophistication, as one can see from the recent theoretical work of Chen *et al.*[1] on the lattice dynamics of ionic-crystal films.

However, while theoretical studies of the phonon and magnon spectrum of finite crystals indicate the presence of a complex variety of surface modes, and also important effects on the eigenvectors and frequency distribution of the bulk modes, until recently direct contact between detailed predictions of the theories and experimental data has been confined to the effect of the surface on quantities that depend on complicated averages over the phonon spectrum. Two examples are the effect of a surface on the phonon specific heat and the determination of the mean-square displacement in the surface from the temperature dependence of the low-energy-electron-diffraction (LEED) intensity.

The study of the energy-loss spectrum of slow electrons scattered from the surface should be, in principle, a powerful probe of the vibrational and magnetic properties of the surface region. However, such experiments are extremely difficult to carry out. If, for example, one wishes to study inelastic scattering of low-energy electrons by phonons utilizing low-energy electrons with energies in the range of 1 to 100 eV, then the incident beam must be extremely monoenergetic. It is very difficult in practice to obtain an electron beam sufficiently monochromatic to enable the study of the extremely small energy transfers involved in electron-phonon or electron-magnon scatterings.

However, Propst and Piper[2] have reported an experimental study of the vibrational modes of hydrogen and other species absorbed on the surface of tungsten by means of low-energy-electron spectroscopy. More recently, Ibach[3,4] has published two very complete experimental investigations of the inelastic scattering of low-energy electrons from the surfaces of ZnO and the (111) surface of silicon. In each case, a discrete-loss (and energy-gain) peak is observed in the energy spectrum of the emerging electrons. These loss and gain peaks are associated with emission and absorption of surface optical phonons by the electron.

In both ZnO and silicon, the scattering is apparently produced by a long-range electric field set up outside the crystal by the surface optical mode. That this is so is evident from the angular distribution of the inelastically scattered electrons.[3-5] In both cases it is observed that the inelastically scattered electrons emerge in a narrow angular cone about the specular direction. This strongly peaked angular distribution indicates that the electron is scattered strongly by surface phonons with small wave vector $\vec{Q}_{\parallel}$; these surface phonons give rise to a long-range electric field that extends well out into the vacuum outside the crystal. Since ZnO is an ionic crystal, it is quite clear that such a long-range electric field should be set up when a long-wavelength surface optical mode is excited. However, silicon presents quite a different state of affairs. The dipole-moment effective charge is zero in the bulk of the silicon crystal, and the $\vec{k}=0$ bulk optical phonon is not infrared (ir) active as a consequence. As Ibach has pointed out,[4] the electric field must then arise by virtue of the low site symmetry of atoms in the surface region. Atoms near the surface may have a nonzero dipole-moment effective charge, since they feel the absence of an inversion center. The motion of these atoms when the surface mode is excited is responsible for the macroscopic electric field near the surface. The fact that atoms in the surface of a nonionic crystal may have a nonzero effective charge played the central role in an earlier theoretical treatment[6] of surface-induced ir absorption in crystals with ir-inactive optical modes at $\vec{k}=0$.

A theory of the inelastic scattering of low-energy electrons from the surface of ionic crystals has been described by Lucas and Šunjić.[5] This theory treats the incident electron as a classical point particle. The electron is allowed to move on a fixed trajectory at constant speed, and the electric field of the electron drives the lattice of the polar crystal. Lucas and Šunjić then obtain an expression for the probability that the incident particle will excite n surface optical phonons. For purposes of analyzing the data of Ibach, the electron is allowed to move along the specular trajectory. The theory is in remarkable quantitative agreement with experiment.[5,7]

Roundy and Mills[8] have discussed the theory of the inelastic scattering of low-energy electrons by phonons of short wavelength. These phonons, by virtue of the conservation of the component of the wave vector parallel to the surface, deflect the electron far from the specular direction. It was assumed that the electrons interact with the ions in the crystal by means of a short-range potential in this study. This work shows by means of a series of model calculations that detailed quantitative information about the lattice dynamics of the crystal surface is contained in the loss spectrum associated with both surface and bulk phonons. The theory of Roundy and Mills is a fully quantum-mechanical one. At this time, no data on the energy spectrum of electrons scattered inelastically through large angles by phonons have been reported, and the theory of Roundy and Mills has no direct bearing on the studies of ZnO and silicon surfaces described above.

The purpose of this paper is to present a quantum-mechanical theory of the inelastic scattering of low-energy electrons from crystal surfaces by long-wavelength surface optical phonons, where the scattering is produced by the long-range electric field described above. There are two purposes in this study. One is to discuss the angular distribution and energy dependence of the cross section for the case where the electrons scatter from a surface of a nonionic crystal such as silicon. As we shall see from the discussion below, the character of the long-wavelength surface optical mode in silicon differs in a qualitative manner from that in ZnO. The difference in character of the two modes is reflected in the angular distribution of the scattered electrons and in the dependence of the total one-phonon cross section on incident electron energy. Finally, we wish to use the magnitude of the scattering cross section reported by Ibach to provide a quantitative measure of the magnitude of the dipole-moment effective charge of the atoms near the surface. The second purpose of the paper is to reexamine from a quantum-mechanical point of view the theory of the one-phonon scattering cross section when the electron scatters from an ionic crystal, such as ZnO. We feel that there are some questions in principle with the approach used by Lucas and Šunjić, and there are also some technical difficulties with their results.

Before we proceed with our treatment, we comment on the approach of Lucas and Šunjić. First of all, there are some technical aspects of their expressions that we find unclear. Their expression for the inelastic-scattering cross section is proportional to a parameter P_0, which is the probability the electron will traverse the classical trajectory with no energy transfer to the lattice. In our view, this parameter is the expression for the specular reflection coefficient provided by their theory, which ignores the quantum-mechanical character of the interaction of the electron with the crystal surface. In their model, P_0 is less than unity only by virtue of the coupling between the electron and the surface optical mode. The actual reflection coefficient differs from unity for very different reasons, of course. For example, when the electron wave enters the crystal, it is damped by electron-electron interactions.[9] In this circumstance the reflection coefficient can be reduced to a value far below unity even in the absence of electron-phonon coupling. At least in metals, it appears that electron-electron interactions play a primary role in determining the value of the reflection coefficient. Lucas and Šunjić argue that P_0 is simply a normalization factor which measures the amount by which the scattered beam is attenuated by the presence of inelastic scattering, and their theory shows the cross section for inelastic scattering to be proportional to the intensity of the elastically scattered beam. For their model, where the reflection coefficient is unity in the absence of electron-phonon coupling, this interpretation of P_0 is equivalent to ours, but it is not obvious to us that one can extend this interpretation to the realistic situation where the reflection coefficient differs from unity for different reasons.

Secondly, the component of the wave vector parallel to the surface of the excitations involved in the interaction process should be conserved, to within a reciprocal-lattice vector. This kinematical feature of the scattering process does not enter a classical point-particle description. If we consider excitation of a surface phonon of wave vector $\vec{Q}_\parallel$ parallel to the surface by the electron within the framework of the Lucas-Šunjić approach and allow the incident electron to follow the appropriate incoming trajectory until it strikes the crystal surface, but take the outgoing trajectory to be arbitrary, then the electron has a finite probability of exciting the surface phonon for any outgoing trajectory, not only the (unique) one determined by considerations of energy and wave-vector conservation.[10] Furthermore, the excitation probability does not peak, if the outgoing trajectory is moved in close to the specular direction.

These difficulties have their origin in the classical description of the electron motion. If one examines the criterion for the validity of such an approach, one can see that a quantum-mechanical description of the scattering process is required. The de Broglie wavelength of the electron is quite small compared to that of the surface optical modes that make the dominant contribution to the cross section. The wavelength of the electron is typically 5 Å, and the phonons involved in the scattering have wavelengths of a few hundred angstroms.[3,4,7] Thus, at first glance, it appears as if there would be little difference between a quantum-mechanical theory and a classical theory, since one may use a wave-packet description of the incident electron and localize the electron well within one phonon wavelength, while still retaining a fairly well-defined energy. This cannot be done, however, since the incident beam is prepared to be a nearly monoenergetic one. If the beam is not very monoenergetic, the small energy transfers involved in the phonon-scattering processes cannot be studied, as we remarked above. Typically, $\Delta E/E_0 \sim 10^{-3}$ in these experiments, where E_0 is the incident energy and ΔE is the uncertainty in the electron's energy. The Heisenberg uncertainty principle then requires that a wave packet with spatial extent Δx no smaller than $\approx 10^3\lambda_0$ can be constructed, where λ_0 is the de Broglie wavelength of the incident electron. Thus, the uncertainty principle forces a quantum-mechanical treatment of the scattering process on us, since the smallest wave packet we can construct within the energy restrictions imposed by preparation of the beam is the order of ten surface-optical-phonon wavelengths. The incident electron must really be a de Broglie wave, and not a classical point particle in a proper theoretical treatment of the scattering process. These are the considerations that lead us to reexamine the Lucas-Šunjić theory for the scattering of an electron from ZnO.

The discussion of the preceding paragraph appears to cast doubts on the results of Lucas and Šunjić. To put the reader at ease, we should remark that for the model examined in this paper, our quantum-mechanical theory reproduces the result of Lucas and Šunjić exactly, provided their parameter P_0 is replaced by the quantum-mechanical reflection coefficient for specular reflection from the crystal surface and the outgoing trajectory is taken to be the specular one. Since these two procedures have been used whenever the theory and experiment have been compared, the excellent quantitative agreement between theory and experiment for the case of ZnO is not altered by this work. In this paper, we consider only the theory of one-phonon scattering, and a study of higher-order processes is currently under way.

The organization of this paper is as follows. In Sec. II we discuss the character of the surface mode in ZnO and silicon, and for each case we derive the form of the contribution of the macroscopic electric field outside the crystal to the electron-phonon interaction. The first part of this discussion (on ZnO) contains no new information, but serves to establish notation. In Sec. III we derive the form of the one-phonon cross section, and discuss its form for the case of ZnO and silicon, with emphasis on the difference between the two cases. We also discuss the kind of information one can obtain from the existing data.

II. INTERACTION BETWEEN ELECTRONS AND LONG-WAVELENGTH SURFACE OPTICAL PHONONS

A. Ionic Crystals

The theory of long-wavelength surface optical phonons in ionic crystals was first discussed by Fuchs and Kliewer,[11] who presented a macroscopic theory of these modes. Subsequently Tong and Maradudin[12] have performed a numerical study of short-wavelength surface modes in such crystals by diagonalizing the dynamical matrix appropriate to a finite slab. The transition region between the long-wavelength regime where the theory of Fuchs and Kliewer is valid and the region of short wavelengths considered by Tong and Maradudin is discussed in the recent work of Chen and his colleagues.[1]

In this work we shall only be concerned with the long-wavelength region, where the ionic solid may be treated as a dielectric medium, with a frequency-dependent dielectric constant

$$\epsilon(\omega)=\epsilon_0+\Omega_p^2/(\omega_0^2-\omega^2) \quad , \tag{1}$$

where ω_0 is the bulk-transverse-optical-phonon frequency and $\Omega_p^2=\omega_l^2-\omega_0^2$, with ω_l the LO-phonon frequency in the bulk.

The interaction energy between an incoming electron and the electric field set up outside the crystal by a lattice vibration of frequency ω_s is given by

$$V(\vec{x},t)=e\,\phi(\vec{x})e^{-i\omega_s t} \quad , \tag{2}$$

where $\phi(\vec{x})$ is the electrostatic potential at point $\vec{x}$, assumed to vary in time like $e^{-i\omega_s t}$. The present discussion neglects retardation. We suppose a phonon has been excited in the medium with a wave vector $\vec{Q}_\parallel$ parallel to the surface. The potential $\phi(\vec{x})$ may then be written

$$\phi(\vec{x})=e^{i\vec{Q}_\parallel\cdot\vec{x}_\parallel}\phi(z)\ , \tag{3}$$

where in this equation and in the remainder of the paper the z direction is normal to the surface and the subscript $\parallel$ denotes either a vector which lies in the plane of the surface or the projection of a general vector onto this plane.

Outside and inside the crystal, $\phi(\vec{x})$ must satisfy Laplace's equation. This means that

$$\phi(z)=\phi_0\,e^{-Q_\parallel|z|}\ , \tag{4}$$

where ϕ_0 is a constant we shall shortly relate to the lattice displacement. Note that the potential must be continuous at the free surface of the dielectric.

We take the crystal to fill the half-space $z<0$. The electric field inside and outside the crystal is given by

$$\vec{E}(\vec{x})=-\nabla\phi(\vec{x})=-Q_\parallel\,\phi_0\,e^{i\vec{Q}_\parallel\cdot\vec{x}_\parallel-Q_\parallel|z|}\,[i\hat{Q}_\parallel-\hat{z}\,\mathrm{sgn}(z)]\ . \tag{5}$$

The tangential component of $\vec{E}(\vec{x})$ is seen to be continuous at the surface, as required by electrostatics. The normal component is not. In fact,

$$E_z(\vec{x})\big|_{z=0^+}=-E_z(\vec{x})\big|_{z=0^-}\ . \tag{6}$$

Since the normal component of the displacement field must be continuous across the boundary, Eq. (6) requires

$$\epsilon(\omega_s)=-1\ . \tag{7}$$

Thus, the potential distribution given by Eq. (3) and Eq. (4) can exist only for one discrete frequency, namely the value of ω_s for which $\epsilon(\omega_s)=-1$. Equation (7) is in fact the eigenvalue condition satisfied by the Fuchs-Kliewer surface mode for the special case where the medium is taken to be semi-infinite.

We next relate the parameter ϕ_0 to the amplitude $\vec{u}$ of the relative motions of the two sublattices of the ionic crystal. When $\epsilon(\omega_s)=-1$, then the total dipole-moment density $P(\vec{x})$ in the medium is

$$\vec{P}(\vec{x})=-(1/2\pi)\,\vec{E}(\vec{x})\ .$$

But the lattice contribution to $\vec{P}(\vec{x})$ is $ne^*\vec{u}(\vec{x})$, where e^* is the dipole-moment effective charge of the $\vec{k}=0$ bulk optical phonon and n is the number of unit cells/unit volume. Thus, we have

$$\vec{E}(\vec{x})=-[4\pi ne^*/(1+\epsilon_0)]\,\vec{u}(\vec{x})\ .$$

We write

$$\vec{u}(\vec{x})=u_0\,(i\hat{Q}_\parallel+\hat{z})\,e^{i\vec{Q}_\parallel\cdot\vec{x}_\parallel} \tag{8}$$

inside the crystal. Then the parameter ϕ_0 is given by

$$\phi_0=[4\pi ne^*/Q_\parallel(1+\epsilon_0)]\,u_0\ .$$

The interaction energy between an electron placed at position $\vec{x}$ at time t, and the surface mode is thus, for $z>0$,

$$V(\vec{x},t)=\frac{4\pi nee^*}{Q_\parallel(1+\epsilon_0)}u_0\,e^{i\vec{Q}_\parallel\cdot\vec{x}_\parallel-Q} \tag{9}$$

We conclude this section by pointing out that no new results are contained here. The form of the interaction energy between an electron and a surface optical phonon (or surface plasmon) has been derived in the earlier work of Lucas, Kartheuser, and Badro.[13] The result in Eq. (9) is equivalent to theirs, provided one associates the amplitude u_0 with the appropriate quantum-mechanical operator.

B. Nonionic Crystals

We now consider the form of the interaction energy between an electron and a surface optical phonon in a nonionic crystal, where the macroscopic field outside of the crystal arises because the atoms in or near the surface feel the absence of an inversion center, as discussed in the Introduction.

Before we proceed to the discussion of the form of the interaction, we present a qualitative discussion of the nature of the surface mode in a crystal such as silicon, where the $\vec{k}=0$ bulk optical phonons are ir inactive.

We shall see in Sec. III of the present paper that the electric dipole moment set up by excitation of the $Q_\parallel=0$ surface optical phonon is quite small for silicon. Thus, the electrostatic contribution to the energy of the wave can be expected to be quite small. On the other hand, an atom in the surface layer is "bonded" to far fewer neighbors than an atom in the bulk. An atom in the (111) surface layer of silicon is missing one first neighbor and three next-nearest neighbors. In the presence of the missing bonds, a surface mode may be split from the bottom of the optical bands and pushed into the gap between the optical and acoustical branches. For a model of a nonionic crystal, surface modes of this type have been studied by Wallis, Mills, and Maradudin.[6] The surface mode is localized to within a small number of atomic layers of the surface for all values of $\vec{Q}_\parallel$, including $\vec{Q}_\parallel = 0$. This behavior is in strong contrast to the behavior exhibited by the Fuchs-Kliewer modes, where as $\vec{Q}_\parallel \to 0$, the mode penetrates very deeply into the crystal. [See Eq. (8) above.] Of course, the model considered by Wallis *et al.* is a crystal very different from silicon. Nonetheless, one can expect the general characteristics of the surface optical mode associated with the (111) surface of silicon to be similar to the mode described in Ref. 6. The main qualitative feature of interest here is that for $\vec{Q}_\parallel = 0$, the displacement field associated with the mode is confined to a small number of layers near the surface and is insensitive to the value of $\vec{Q}_\parallel$, so long as $\vec{Q}_\parallel$ is close to the center of the Brillouin zone appropriate to the surface layer.

In order to stress the similarity of the surface mode studied by Wallis *et al.*[6] to that observed in silicon, note that there is indeed a gap between the acoustical and optical branches of silicon for propagation in the (111) direction normal to the surface.[14] This gap is very similar to the one present in Fig. 2 of Ref. 6, at $\phi_1 = 0$. In silicon the gap extends from $(0.71 \pm 0.02)\omega_0$ to $(0.82 \pm 0.02)\omega_0$, where ω_0 is the Raman frequency of silicon. The surface-optical-mode frequency observed by Ibach appears to fall close to the gap, since its frequency is $\omega_s = 0.86\omega_0$.

We now calculate the interaction energy between an electron and the electric field set up by a surface mode of the type described in the preceding paragraphs. When the mode is excited, there will be a two-dimensional wavelike dipole layer induced in the surface region of the crystal. The thickness of this layer is microscopic, the order of a few lattice constants at most. The thickness of the dipole layer can be regarded as independent of the wavelength of the surface optical phonon, in contrast to the situation in ionic crystals. The interaction energy of an electron with the wave is still given by Eq. (2), and we next determine the form of $\phi(\vec{x})$.

First consider the potential generated by a single electric dipole with dipole moment $\vec{P}$ placed on the surface of a dielectric substrate with dielectric constant ϵ. The form of the potential is easily constructed by using the image-charge method of electrostatics. We find the potential $\Phi(\vec{x})$ produced by the dipole is

$$\Phi(\vec{x}) = \frac{2\epsilon}{1+\epsilon} \frac{\vec{P}_\perp \cdot (\vec{x} - \vec{r}_\parallel)}{|\vec{x} - \vec{r}_\parallel|^3} + \frac{2}{1+\epsilon} \frac{\vec{P}_\parallel \cdot (\vec{x} - \vec{r}_\parallel)}{|\vec{x} - \vec{r}_\parallel|^3}, \qquad (10)$$

where $\vec{r}_\parallel$ specifies the location of the dipole on the surface and $\vec{P}_\perp$, $\vec{P}_\parallel$ are the components of the dipole moment perpendicular and parallel, respectively, to the surface.

Now divide the surface layer of the crystal up into (two-dimensional) unit cells, and let there be n_0 unit cells/cm^2. Let $\vec{P}_l$ be the electric dipole moment induced in unit cell $\vec{l}$, as a result of excitation of the surface optical phonon. Then

$$\vec{P}_l = e^{i\vec{Q}_\parallel \cdot \vec{r}_l} \vec{P},$$

where $\vec{Q}_\parallel$ is the wave vector of the surface phonon. Then the potential outside the crystal is

$$\phi(\vec{x}) = \frac{2\epsilon}{1+\epsilon} \sum_{\vec{l}} \frac{\vec{P}_\perp \cdot (\vec{x} - \vec{r}_l)\, e^{iQ_\parallel \cdot r_l}}{|\vec{x} - \vec{r}_l|^3} + \frac{2}{1+\epsilon} \sum_{\vec{l}} \frac{\vec{P}_\parallel \cdot (\vec{x} - \vec{r}_l)\, e^{i\vec{Q}_\parallel \cdot \vec{r}_l}}{|\vec{x} - \vec{r}_l|^3}. \qquad (11)$$

The sums in Eq. (11) may be carried out in closed form.[15] However, we are interested only in the long-range part of the potential present for small $\vec{Q}_\parallel$. This portion may be computed by replacing the sum over the sites in the surface by an integration. The integrations are easily carried out, and one finds

$$\phi(\vec{x}) = \frac{4\pi n_0 \epsilon}{1+\epsilon} e^{i\vec{Q}_\parallel \cdot \vec{x}_\parallel} e^{-Q_\parallel z} \left(\vec{P}_\perp - \frac{i}{\epsilon} \hat{Q}_\parallel \cdot \vec{P}_\parallel \right), \qquad (12)$$

where $\hat{Q}_\parallel$ is a unit vector in the direction of $\vec{Q}_\parallel$.

Notice that the interaction energy obtained from Eq. (12) and that in Eq. (9) exhibit the same spatial dependence. This, of course, is a consequence of the fact that outside the crystal $\nabla^2 \phi = 0$, while at the same time ϕ is proportional to $e^{iQ_\parallel \cdot x_\parallel}$. We may summarize the results of this section by noting that we may write

$$V(\vec{x}, t) = \Delta_{\vec{Q}_\parallel}(z)\, e^{iQ_\parallel \cdot x_\parallel} e^{-i\omega_s t} + \text{c. c.}, \qquad (13)$$

where for the ionic crystal

$$\Delta_{Q_\parallel}(z) = [4\pi n e e^* u_0 / Q_\parallel (1 + \epsilon_0)]\, e^{-Q_\parallel z} \qquad (14a)$$

and for the nonionic or covalent crystal

$$\Delta_{Q_\parallel}(z) = \frac{4\pi n_0 e \epsilon}{1+\epsilon} e^{-Q_\parallel z} \left(\vec{P}_\perp - \frac{i}{\epsilon} \hat{Q}_\parallel \cdot \vec{P}_\parallel \right). \qquad (14b)$$

Equations (14) are valid only for z outside the crystal.

It should be noted that the contribution to $\Delta_{Q_\parallel}(z)$ in Eq. (14b) from the component of the dipole moment parallel to the surface is smaller than that normal to the surface by the factor ϵ^{-1}. Since $\epsilon \cong 12$ for silicon, this will lead us to suggest that atomic motions normal to the surface are the source of the scattering observed in silicon by Ibach.

III. THEORY OF INELASTIC SCATTERING OF LOW-ENERGY ELECTRONS BY SURFACE OPTICAL MODES

In this section we derive the form of the cross section for inelastic scattering of low-energy electrons by surface optical phonons. The interaction potential we employ for the two cases of interest will be those derived in Sec. II.

We make two remarks about the approach we will use. In Eq. (13) and Eqs. (14) we give the form of the interaction potential and a surface optical phonon with wave vector $\vec{Q}_{\parallel}$ parallel to the surface. The parameters u_0 and $\vec{P}$ that appear in Eqs. (14) should be taken to be the appropriate quantum-mechanical operators, each involving the boson annihilation and creation operators appropriate to the surface phonon. In order to keep the equations of the present as simple as possible, we treat these two quantities as c numbers for the moment, and the correspondence principle will be involved at a later point in the discussion in order to obtain the fully quantum-mechanical expressions for the cross section. For the case considered here, where only the one-phonon cross section is examined, this procedure is quite straightforward and simplifies the intermediate equations. We also consider the scattering produced by one single phonon, and then construct the form of the differential cross section per unit solid angle from this result.

If $\psi(x, t)$ denotes the wave function of the electron, then we are led to examine the Schrödinger equation (with $\hbar = 1$):

$$\left(-\frac{\nabla^2}{2m} + V_0(x) + \Delta_{\vec{Q}_{\parallel}}(z)\, e^{iQ_{\parallel}\cdot x_{\parallel}} e^{i\omega_s t} + \text{c. c.}\right)\psi(\vec{x}, t) = i\,\frac{\partial\psi(\vec{x}, t)}{\partial t} \quad . \tag{15}$$

In Eq. (15) $V_0(\vec{x})$ is the potential associated with the static crystal, which fills the half-plane $z < 0$. Since the scattering processes we consider are produced by the long-range electric field outside the crystal, we expect the general form of the cross section to be independent of the detailed structure for $V_0(\vec{x})$. For this function, we thus take the very simple functional form

$$V_0(\vec{x}) = V_0\,\theta(-z)\ , \tag{16}$$

i. e., the crystal is presumed to present a simple step potential to the electron. The parameter V_0 will be assumed to be complex, with the imaginary part assumed to have its origin in the damping provided by electron-electron interactions. The reflection coefficient from the static potential barrier will thus be less than unity for the model. While the choice for $V_0(x)$ represents a severe simplification of the actual state of affairs, it does have the virtue of allowing very simple closed expressions to be obtained in the discussion below.

We shall now derive the amplitude of the scattered wave, using a technique very similar to that employed in the theory of Raman scattering of light from opaque materials.[16]

The wave function will first be Fourier transformed in a manner convenient for the discussion of surface problem:

$$\psi(x, t) = \int \frac{d^2k_{\parallel}\,d\omega}{(2\pi)^3}\ \psi(\vec{k}_{\parallel}\,\omega;\ z)\, e^{ik_{\parallel}\cdot x_{\parallel}} e^{-i\omega t}\ . \tag{17}$$

The Schrödinger equation then assumes the form

$$\left(\frac{k_{\parallel}^2}{2m} - \omega - \frac{1}{2m}\,\frac{\partial^2}{\partial z^2} + V_0\,\theta(-z)\right)\psi(\vec{k}_{\parallel}\,\omega\,;z) = -\Delta_{Q_{\parallel}}(z)\,\psi(\vec{k}_{\parallel} - \vec{Q}_{\parallel};\,\omega - \omega_s) - \Delta^*_{Q_{\parallel}}(z)\,\psi(\vec{k}_{\parallel} + \vec{Q}_{\parallel};\,\omega + \omega_s)\ . \tag{18}$$

We now introduce a Green's function, defined by the equation

$$\left(-\frac{1}{2m}\,\frac{\partial^2}{\partial z^2} + \frac{k_{\parallel}^2}{2m} + V(z) - \omega\right) G(\vec{k}_{\parallel}\omega\,; zz') = \delta(z - z')\ . \tag{19}$$

As $z \to +\infty$ for fixed z', we require $G(\vec{k}_{\parallel}\omega;\ zz')$ to satisfy an outgoing-wave boundary condition, and $G(\vec{k}_{\parallel}\omega; zz') \to 0$ as $z \to -\infty$. With the aid of the Green's function, Eq. (18) becomes

$$\begin{aligned}\psi(\vec{k}_{\parallel}\omega\,; z) = \psi_0(\vec{k}_{\parallel}\omega\,; z) &- \int_{-\infty}^{+\infty} dz'\, G(\vec{k}_{\parallel}\omega;\ zz')\,\Delta_{Q_{\parallel}}(z') \\ &\times \psi(\vec{k}_{\parallel} - \vec{Q}_{\parallel};\,\omega - \omega_s,\, z') - \int_{-\infty}^{+\infty} dz'\, G(\vec{k}_{\parallel}\,\omega\,; zz') \\ &\times \Delta^*_{Q_{\parallel}}(z')\,\psi(\vec{k}_{\parallel} + \vec{Q}_{\parallel};\ \omega + \omega_s,\, z')\ ,\end{aligned} \tag{20}$$

where $\psi_0(\vec{k}_{\parallel}\,\omega;\ z)$ is a solution of Eq. (18) with $\Delta_{Q_{\parallel}}(z) = 0$. The solution $\psi_0(\vec{k}_{\parallel}\,\omega;\ z)$ describes specular reflection of the electron from the surface.

In order to solve Eq. (20), we need a form for the Green's function that appears in the kernel of the integrals. For our model, an explicit form for this function is easily obtained. Define a quantity

$$\gamma = (k_{\parallel}^2 + 2m(V_0 - \omega))^{1/2} \tag{21a}$$

and

$$k_z = +\,(2m\omega - k_{\parallel}^2)^{1/2}\ . \tag{21b}$$

Since V_0 is complex, γ is complex also. We always choose that square root which gives γ a positive real part. For the values of $\vec{k}_{\parallel}$ and ω of interest, k_z will be real. We choose the positive root in Eq. (21b). Then we introduce two solutions of the homogeneous part of Eq. (18):

$$\psi^-(k_{\parallel}\omega, z) = \begin{cases} e^{-ik_z z} + R\,e^{ik_z z}\ , & z > 0 \\ T\,e^{+\gamma z}\ , & z < 0 \end{cases} \tag{22a}$$

$$\psi^+(k_{\parallel}\omega, z) = \begin{cases} e^{+ik_z z}, & z > 0 \\ \cosh(\gamma z) + i(k_z/\gamma)\sinh(\gamma z), & z < 0\ . \end{cases} \tag{22b}$$

In Eq. (22a) we have

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

and $T = 1 + R$. The Green's function may be simply expressed in terms of ψ^+ and ψ^-:

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

We now return to the solution of Eq. (20). The right-hand side consists of a sum of the specularly reflected wave [represented by $\psi_0(\vec{k}_{\parallel}\,\omega,\,z)$] and the scattered wave $\psi_s(k_{\parallel}\,\omega\,;\,z)$. An explicit expression for $\psi_s\,(\vec{k}_{\parallel}\,\omega\,;\,z)$ is

$$\psi_s(\vec{k}_{\parallel}\,\omega\,;\,z)=-\int_{-\infty}^{+\infty}dz'\,G(\vec{k}_{\parallel}\,\omega,\,zz')\,\Delta_{Q_{\parallel}}(z')$$
$$\times\,\psi\,(\vec{k}_{\parallel}-\vec{Q}_{\parallel},\;\omega-\omega_s,\,z')-\int_{-\infty}^{+\infty}dz'\,G(\vec{k}_{\parallel}\,\omega,\,zz')$$
$$\times\,\Delta^{*}_{\vec{Q}_{\parallel}}(z')\,\psi\,(\vec{k}_{\parallel}+\vec{Q}_{\parallel},\;\omega+\omega_s,\,z')\;. \tag{23}$$

We shall calculate the amplitude of the scattered wave to first order in $\Delta_{Q_{\parallel}}(z)$ in this paper. This may be done simply by replacing the functions $\psi(\vec{k}_{\parallel}\pm\vec{Q}_{\parallel},\;\omega\pm\omega_s,\,z')$ on the right-hand side of Eq. (23) by the amplitude ψ_0 of the incident wave in Eq. (20). Then the first term in Eq. (23) describes the contribution to the amplitude of the scattered wave from processes in which the electrons absorb a surface phonon, and the second describes the contribution from processes in which a phonon is emitted. We shall keep only the first term, and note that the cross section for emission and absorption may be related by considerations of detailed balance. Upon inserting the explicit form of the Green's function into the first term of Eq. (23), one finds

$$\psi_s(\vec{k}_{\parallel}\omega,\,z)=-\,i\,(m/k_z)\,\psi^{+}(\vec{k}_{\parallel}\omega;\,z)\int_{-\infty}^{z}dz'\,\psi^{-}(\vec{k}_{\parallel}\omega,\,z')$$
$$\times\,\Delta_{Q_{\parallel}}(z')\;\psi_0\,(\vec{k}_{\parallel}-\vec{Q}_{\parallel},\,\omega-\omega_s,\,z')-i\,(m/k_z)\,\psi^{-}(\vec{k}_{\parallel}\omega;\,z)$$
$$\times\int_{z}^{\infty}dz'\psi^{+}\,(\vec{k}_{\parallel}\omega,\,z')\,\Delta_{\vec{Q}_{\parallel}}(z')\,\psi_0(\vec{k}_{\parallel}-\vec{Q}_{\parallel};\,\omega-\omega_s,\,z')\;.$$

To calculate the cross section, only the form of the wave function far from the crystal is of interest. Thus we let $z\to\infty$, and note the second term drops out, because $\Delta_{\vec{Q}_{\parallel}}(z')\to 0$ exponentially fast. Thus, far from the crystal,

$$\psi_s(\vec{k}_{\parallel}\omega,\,z)=-i(m/k_z^{(s)})e^{+ik^{(s)}z}\int_{-\infty}^{+\infty}dz'\psi^{-}(k_{\parallel}\omega,\,z')$$
$$\times\,\Delta_{Q_{\parallel}}(z')\,\psi_0(k_{\parallel}-Q_{\parallel},\,\omega-\omega_s,z')\,. \tag{24}$$

We have appended the superscript (s) to k_z, to denote that this quantity is the z component of the wave vector of the outgoing scattered wave.

The integral in Eq. (24) extends over all values of z'. However, it is easily seen that the only appreciable contribution occurs from the region $z'>0$. This is because $\psi_0\,(\cdots,z')$ and $\psi^{-}(\cdots,z')$ fall to zero rapidly as z' is moved into the crystal. The region $z'<0$ contains a contribution only from a thin layer with thickness the order of the electron mean-free path, given as the inverse of $\mathrm{Re}(\gamma)$ in our model. On the other hand, $\psi^{-}(\cdots,z')$ and $\psi_0(\cdots,z')$ have a wavelike character for $z'>0$, and the integral converges by virtue of the cutoff provided by $\Delta_{\vec{Q}_{\parallel}}(z')$, which is proportional to $e^{-Q_{\parallel}z'}$. Since the surface phonons of interest have wavelengths long compared to the depth of penetration of the electron in the crystal, it follows that the lower limit of the integral may be replaced by zero to a good approximation.

Furthermore, we take $\psi_0(\vec{k}_{\parallel},\,\omega,\,z')$ to represent an electron of well-defined wave vector and energy. For the region $z>0$,

$$\psi_0(\vec{k}_{\parallel}\omega,\,z')=(2\pi)^3\,\delta(\vec{k}_{\parallel}-\vec{k}_{0_{\parallel}})\,\delta(\omega-E^{(0)})$$
$$\times\,(e^{-ik_{0z}z}+R_I e^{+ik_{0z}z})\,.$$

Furthermore, we write

$$\Delta_{Q_{\parallel}}(z)=\Delta(\vec{Q}_{\parallel})\,e^{-Q_{\parallel}z}\,. \tag{25}$$

Equation (24) then becomes

$$\psi_s(\vec{k}_{\parallel}\omega;\,z)=-\,i\,(m/k_z^{(s)})e^{ik_z^{(s)}z}\quad(2\pi)^3\,\delta(\vec{k}_{\parallel}-\vec{k}_{0_{\parallel}}-\vec{Q}_{\parallel})$$
$$\times\;\delta(\omega-\omega_s-E^{(0)})\,\Delta(\vec{Q}_{\parallel})\int_0^{\infty}dz'\,(e^{-ik_z^{(s)}z'}+R_s\,e^{+ik_z^{(s)}z'})$$
$$\times\;e^{-Q_{\parallel}z'}\,(e^{-ik_{0z}z'}+R_I\,e^{+ik_{0z}z'}\,)\,.$$

The integral in this result is trivially performed, to yield

$$\psi_s(k_{\parallel}\omega;\,z)=-\,i(2\pi)^3\,(m/k_z^{(s)})\,e^{ik_z^{(s)}z}\,\Delta(\,Q_{\parallel})$$
$$\times\;\delta\,(\vec{k}_{\parallel}-\vec{k}_{0\,\parallel}-\vec{Q}_{\parallel}\,)\;\delta(\omega-\omega_s-E^{(0)})$$
$$\times\left(\frac{1}{Q_{\parallel}+ik_z^{(s)}+ik_{0z}}+\frac{R_s}{Q_{\parallel}+ik_{0z}-ik_z^{(s)}}+\frac{R_I}{Q_{\parallel}+ik_z^{(s)}-ik_{0z}}\right.$$
$$\left.+\,\frac{R_sR_I}{Q_{\parallel}-ik_z^{(s)}-ik_{0z}}\right)\,. \tag{26}$$

Consider the relative order of magnitude of the terms in Eq. (26). The de Broglie wavelength of the incident electron is very short, so both $k_s^{(s)}$ and k_{0z} will be large compared to $Q_{\parallel}$, if we confine attention to the scattering produced by long-wavelength surface modes. It is then clear that the second and third terms of Eq. (26) will give contributions to the cross section which peak sharply about the specular direction, where $k_z^{(s)}\approx k_{0z}$. The first and fourth terms give rise to a broad background, which varies smoothly with scattering angle. The broad background is weak compared to the small-angle scattering. Since we are interested only in the strong scattering that occurs near the specular direction, we retain only the second and third terms in Eq. (26). Indeed, the present theory is not expected to give a meaningful result for large scattering angles, since one requires the form of the perturbing potential close to the crystal surface to calculate this part. Furthermore, since the energy and outgoing direction of the incident and scattered electron are nearly identical for the small-angle scattering, R_s and R_I will be taken equal.

Note that with these approximations the amplitude of the inelastic wave is proportional to that of the elastically scattered specular beam. As one can see from the preceding paragraph, this proportionality holds only when scattering near the specular direction dominates the cross section.

Before we proceed, we note that the four terms of Eq. (26) have a simple physical significance, as illustrated in Fig. 1. The second term describes a process in which the electron is kicked onto the outgoing trajectory before it strikes the crystal surface [Fig. 1(a)]; the third [Fig. 1(b)] describes a process in which the electron enters on the incident trajectory, reflects off the surface, and is knocked onto the outgoing trajectory after reflection. The first term corresponds to Fig. 1(c), where the electron is scattered onto the outgoing trajectory before it strikes the crystal surface. Finally, the final term describes an interaction that knocks the electron onto the incoming portion of the scattered trajectory, after its first reflection off the surface. The total trajectory is the "two-bounce" trajectory shown in Fig. 1(d). Note that for the processes shown in Figs. 1(a) and 1(d), even though the scattered trajectory may lie close to the incident one, a deflection through a large angle is required in the scattering process.

If the approximate form of $\psi_s(\vec{k}_\parallel\omega;z)$ obtained from Eq. (26), after the first and fourth terms are neglected, is substituted back into Eq. (17), for the outgoing wave we obtain

$$\psi_s(\vec{x},t) = -\frac{2imR\,\Delta(\vec{Q}_\parallel)}{k_z^{(s)}}\,\frac{Q_\parallel}{Q_\parallel^2+(\Delta k_z)^2}\,e^{i\vec{k}^{(s)}\cdot\vec{r}}\,e^{-iE^{(s)}t}\,, \tag{27a}$$

where $R=R_s\cong R_I$ is the reflection coefficient,

$$\Delta k_z = k_{0z}-k_z^{(s)}\,, \quad \vec{k}_{0z}=\vec{k}_z^{(s)}+\vec{Q}_\parallel\,, \tag{27b}$$

and

$$E^{(0)}=E^{(s)}+\omega_s\,. \tag{27c}$$

Let j_s denote the magnitude of the probability current associated with the outgoing wave and j_I that associated with the incident wave. Since $k_0 \approx k^{(s)}$, a short calculation shows

$$\frac{j_s}{j_I}=\frac{8|R|^2}{V_\perp^2}\,\frac{|\Delta(Q_\parallel)|^2Q_\parallel^2}{[Q_\parallel^2+(\Delta k_z)^2]^2}\,, \tag{28}$$

where we have replaced $k_z^{(s)}$ by $mV_\perp^{(s)}\approx mV_{0\perp}=mV_\perp$.

Equation (28) gives the scattering efficiency associated with one particular surface optical phonon. The scattering efficiency per unit solid angle can be determined as follows. Consider the scattering produced by the modes that lie in the area $d^2Q_\parallel$ of the $Q_\parallel$ plane. The total number of such modes is $Ad^2Q_\parallel/4\pi^2$, where A is surface area. The total outgoing current produced by the modes that lie within the area $d^2Q_\parallel$ may be found by multiplying Eq. (28) by $Ad^2Q_\parallel/4\pi^2$. Suppose these modes scatter the electrons in to the solid angle $d\Omega$. The scattering efficiency per unit solid angle is then

$$\frac{dS}{d\Omega}=\frac{2}{\pi^2}\,\frac{|R|^2}{V_\perp^2}\,\frac{|\Delta(Q_\parallel)|^2Q_\parallel^2}{Q_\parallel^2+(\Delta k_z)^2}\,\frac{d^2Q_\parallel}{d\Omega}\,. \tag{29}$$

The ratio $d^2Q_\parallel/d\Omega$ is readily calculated by means of an argument presented elsewhere.[16] One finds

$$\frac{d^2Q_\parallel}{d\Omega}=k_s^2\cos\theta_s\,, \tag{29a}$$

where θ_s is the angle between the scattered beam and the normal to the surface. Then, finally, for scattering near the specular direction,

$$\frac{dS}{d\Omega}=\frac{2A}{\pi^2}\,|R|^2\,\frac{|\Delta(Q_\parallel)|^2}{\cos\theta}\,\frac{Q_\parallel^2}{[Q_\parallel^2+(\Delta k_z)^2]^2}\,, \tag{30}$$

where we write $V_\perp=V_0\cos\theta$, and θ measures the angle made by the incident beam and the normal of the crystal surface.

We now turn to the kinematics of the scattering process to first express the right-hand side of Eq. (30) entirely in terms of $\vec{Q}_\parallel$, then finally in terms of a set of angles which define the direction of the outgoing beam relative to the specular beam.

Consider energy conservation, and suppose $|\vec{Q}|_\parallel \ll |\vec{k}_{0\parallel}|$. Then we have

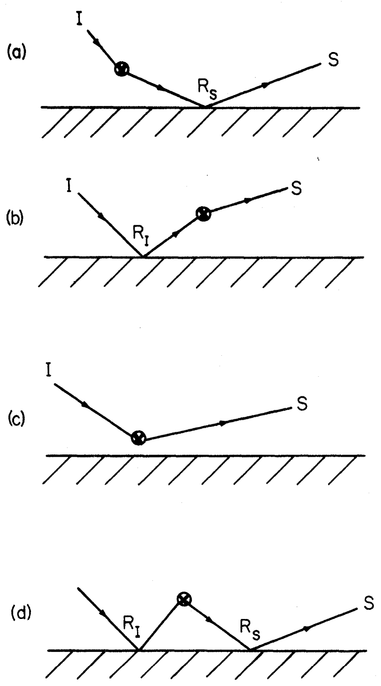

FIG. 1. Schematic representation of the four terms in Eq. (26): (a) the second term; (b) the third term; (c) the first term; (d) the fourth term.

$$E^{(s)}=\frac{(\vec{k}_{0\parallel}+\vec{Q}_{\parallel})^2}{2m}+\frac{(k_{0z}+\Delta k_z)^2}{2m}\cong E^{(0)}+\vec{V}_{\parallel}\cdot\vec{Q}_{\parallel}+V_{\perp}\,\Delta k_z$$
$$=E^{(0)}+\omega_s\ ,$$

where $\vec{V}_{\parallel}$ is the component of the electron's velocity in the plane of the surface. Thus we have

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

and Eq. (30) may be written

$$\frac{dS}{d\Omega}=\frac{4A}{\pi^2}mE^{(0)}|\Delta(Q_{\parallel})|^2|R|^2\cos\theta$$
$$\times\left(\frac{V_{\perp}^2Q_{\parallel}^2}{[V_{\perp}^2Q_{\parallel}^2+(\omega_s-\vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2]^2}\right)\ . \qquad (31)$$

From the form of the quantity in large parentheses in Eq. (31), one can begin to see the result of Lucas and Šunjić emerging from the present work.

We define the direction of the scattered beam by introducing the two angles ψ and φ indicated in Fig. 2. The x and y axes are oriented so the specular trajectory lies in the x-z plane. The angle between $\vec{k}_0$ and $\vec{k}_s$ is ψ, and only the limit $\psi\ll 1$ is of interest. The angle between the plane which contains $\vec{k}_0$ and $\vec{k}_s$ and the x-z plane is denoted by φ.

From the geometry of Fig. 2, combined with conservation of energy and the component of wave vector parallel to the surface, we find (for $\psi\ll 1$)

$$Q_{\parallel}^y=k_0\psi\sin\varphi\ , \qquad (32a)$$

$$Q_{\parallel}^x=(\omega_s/V_0)\sin\theta-k_0\psi\cos\theta\cos\varphi\ , \qquad (32b)$$

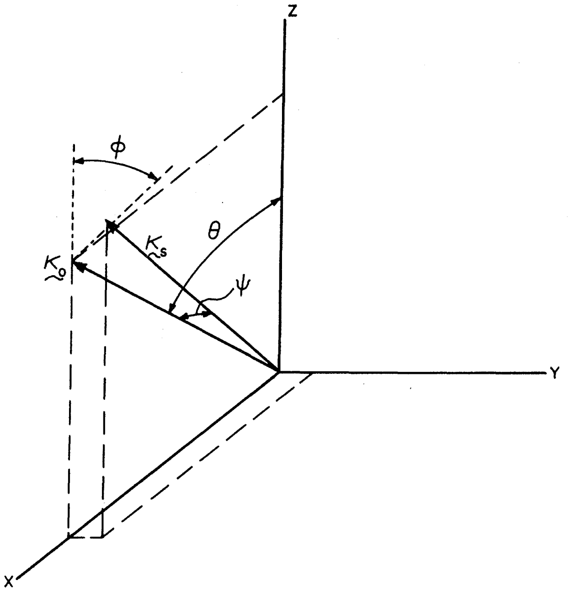

FIG. 2. Angles ψ and φ used to define the direction of the scattered beam.

and

$$\Delta k_z=(\omega_s/V_0)\cos\theta+k_0\psi\sin\theta\cos\varphi\ , \qquad (32c)$$

where k_0 and V_0 are the wave vector and velocity of the incident electron, respectively; it then follows that

$$Q_{\parallel}^2+(\Delta k_z)^2=k_0^2[\psi^2+(\omega_s/2E^{(0)})^2]$$

and

$$Q_{\parallel}^2=k_0^2\left(\cos\varphi\cos\theta\,\psi-\frac{\omega_s}{2E^{(0)}}\sin\theta\right)^2+k_0^2\sin^2\varphi\,\psi^2\ .$$

Thus, $dS/d\Omega$ may be written in the form

$$\frac{dS}{d\Omega}=\frac{A}{\pi^2}\frac{m|\Delta(\psi,\varphi)|^2}{E^{(0)}\cos\theta}|R|^2$$
$$\times\frac{[\cos\varphi\cos\theta\,\psi-(\omega_s/2E^{(0)})\sin\theta]^2+\sin^2\varphi\,\psi^2}{[\psi^2+(\omega_s/2E^{(0)})^2]^2}\ . \qquad (33)$$

Equation (33) is the final result of the present section. One can see that the scattering cross section does indeed contain a strong peak about the specular direction. The cross section falls off rapidly when $\psi\gg\omega_s/2E^{(0)}$. Before we can discuss the detailed behavior of the cross section, we need information about $|\Delta(\psi,\varphi)|^2$. We thus must consider the ionic and covalent crystal separately, as we have seen in Sec. II. We now turn to these two cases.

Before we proceed, note that $dS/d\Omega$ is proportional to the intensity of the *scattered* beam. This proportionality is well supported by the data on ZnO.[7] The validity of this relation depends on the small contribution provided by the terms illustrated in Figs. 1(a) and 1(d), as remarked earlier.

A. Application of Theory to Ionic Crystals

The central question in this case is the relationship of the present results to the earlier work of Lucas and co-workers. We shall examine only the expression for the total cross section. Thus, we want to compute the integral of $dS/d\Omega$ over all solid angle to compare with their results. This may be done conveniently by utilizing Eq. (31).

This gives for the total scattering efficiency

$$S=\frac{4A}{\pi^2}\frac{E^{(0)}}{m}|R|^2\cos\theta\int d\Omega\,|\Delta(Q_{\parallel})|^2$$
$$\times\frac{V^2{}_{\perp}Q_{\parallel}{}^2}{[V_{\perp}^2Q_{\parallel}^2+(\omega_s-\vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2]^2}\ .$$

This may be converted to an integral over $\vec{Q}_{\parallel}$ by the use of Eq. (29a):

$$S=\frac{2A}{\pi^2}|R|^2\int d^2Q_{\parallel}\,|\Delta(Q_{\parallel})|^2$$
$$\times\frac{V_{\perp}^2Q_{\parallel}^2}{[V_{\perp}^2Q^2+(\omega_s-\vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2]^2}\ . \qquad (34)$$

From Sec. II, we have

$$|\Delta(Q_{\parallel})|^2=\frac{16\pi^2 n^2 e^2 e^{*2}}{Q_{\parallel}^2(1+\epsilon_0)^2}\;|u_0(Q_{\parallel})|^2\,,$$

where $u_0(Q_{\parallel})$ is the amplitude appropriate to the surface phonon of wave vector $\vec{Q}_{\parallel}$.

The coordinate $\vec{u}$ is the normal coordinate associated with optical motion of the lattice. If we consider a lattice consisting of two ionic species, one of mass M_1 and one of mass M_2, the optical displacement of atoms in the unit cell is

$$\vec{u}(l)=\vec{u}_1(\vec{l})-\vec{u}_2(\vec{l})$$
$$=\sum_n \frac{1}{(2\omega_n)^{1/2}}\left(\frac{\vec{e}_n(\vec{l}1)}{(M_1)^{1/2}}-\frac{\vec{e}_n(\vec{l}2)}{(M_2)^{1/2}}\right)(a_n+a_n^{+})\,.$$

In this expression, n is a normal-mode index. When optical motion of the lattice is excited, the center of mass of the unit cell remains at rest, so

$$(M_1)^{1/2}\hat{e}_n(\vec{l}1)+(M_2)^{1/2}\hat{e}_n(\vec{l}2)=0 \tag{35}$$

for such a mode. The eigenvector of the model must be normalized, so

$$\sum_{\vec{l}}\,[\,|\vec{e}_n(l1)|^2+|\vec{e}_n(\vec{l}2)|^2]=1.$$

For the Fuchs-Kliewer surface mode, we have

$$\hat{e}(\vec{l}1)=C\,(\hat{x}-i\hat{z})e^{i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel}}e^{-Q_{\parallel}z}\,,$$

as we have seen, with $\hat{e}(\vec{l}z)$ determined by Eq. (35). The constant C is uniquely determined from the normalization condition:

$$C=[M_2Q_{\parallel}a_0/N_s(M_1+M_2)]^{1/2}\,,$$

where a_0 is the separation between successive layers. Then, if the sum over s is restricted to the Fuchs-Kliewer modes only, and μ is the reduced mass of the unit cell,

$$\vec{u}(\vec{l})=\sum_{\vec{Q}_{\parallel}}\left(\frac{Q_{\parallel}a_0}{2N_s\,\omega_s\mu}\right)^{1/2}(\hat{x}-i\hat{z})e^{iQ_{\parallel}\cdot l_{\parallel}}e^{-Q_{\parallel}l}$$
$$\times\,(a_{Q_{\parallel}}+a^{+}_{-Q_{\parallel}})\,.$$

The correspondence principle states that the classical amplitude $|u_0(Q_{\parallel})|^2$ that appears in Eq. (34) is to be replaced by the coefficient of $(\hat{x}-i\hat{z})$ in the matrix element of $\vec{u}(0)$ between states with n_s and (n_s-1) phonons of wave vector $\vec{Q}_{\parallel}$:

$$|u(\vec{Q}_{\parallel})|^2\rightarrow(Q_{\parallel}a_0/2N_s\omega_0N)n_s\,,$$

where in thermal equilibrium, $n_s=(e^{\omega_s/k_BT}-1)^{-1}$ independent of $\vec{Q}_{\parallel}$. Then Eq. (34) becomes

$$S=16|R|^2\frac{n^2e^2e^{*2}A_ca_0}{\omega_s\mu(1+\epsilon_0)^2}\,n_s\int\frac{d^2Q_{\parallel}\,V_{\perp}^2Q_{\parallel}}{[V_{\perp}^2Q_{\parallel}^2+(\omega_s-\vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2]^2}\,,$$

where A_c is the area of the unit cell in the surface of the crystal. The quantity A_ca_0 may be identified with the volume of the unit all in the bulk. Thus

$$S=\frac{16|R|^2ne^2e^{*2}}{\omega_s\mu(1+\epsilon_0)^2}\,n_s\int\frac{d^2Q_{\parallel}\,V_{\perp}^2Q_{\parallel}}{[V_{\perp}^2Q_{\parallel}^2+(\omega_s-\vec{V}_{\parallel}\cdot\vec{Q}_{\parallel})^2]^2}\,.$$

Now introduce the ion plasma frequency ω_p, defined by

$$\omega_p^2=4\pi ne^{*2}/\mu\,.$$

Then inserting a missing factor of $\hbar$, we have

$$S=|R|^2\frac{4}{\pi}\frac{\omega_p^2e^2}{\hbar\omega_s(1+\epsilon_0)^2}\,n_s\int\frac{d^2Q_{\parallel}V_{\perp}^2Q_{\parallel}}{[V_{\perp}^2Q_{\parallel}^2+(\omega_s-\vec{Q}_{\parallel}\cdot\vec{V}_{\parallel})^2]^2}\,. \tag{36}$$

The result displayed in Eq. (36) may now be conveniently compared with that of Lucas and Šunjić. If, in their classical treatment, the electron is allowed to follow the specular trajectory after reflection from the crystal surface, and if their parameter P_0 is replaced by the quantum-mechanical reflection coefficient $|R|^2$, then our result is identical to their expression for the one-phonon cross section.

We conclude this section by quoting the expression for the total scattering cross section obtained from Eq. (36)[5,7]:

$$S=\pi|R|^2[e^2\omega_p^2/\hbar\omega_s^2V_{\perp}(1+\epsilon_0)^2]\,. \tag{37}$$

A complete and careful review of the remarkable agreement between the Lucas-Šunjić theory and the experimental data on ZnO has been given by Ibach.[7]

B. Application of the Theory to Nonionic Crystals

We start with Eq. (33) and obtain the form of $|\Delta|^2$ from the earlier discussion. From Eq. (14b),

$$|\Delta(\vec{Q})_{\parallel}|^2=\frac{16\pi^2n_0^2e^2\epsilon^2}{(1+\epsilon)^2}\left(P_{\perp}^2+\frac{1}{\epsilon^2}(\hat{Q}_{\parallel}\cdot\vec{P}_{\parallel})^2\right)\,. \tag{38}$$

From Eq. (38), one sees that the contribution to the cross section from atomic motions normal to the surface is larger by a factor of ϵ^2 than the contribution from that parallel to the surface. Since $\epsilon=12$ for silicon, the second term is much smaller than the first for this crystal. In the discussion below, we shall drop the term proportional to $P_{\parallel}^2$, upon the assumption that the surface phonon involves motions normal to the surface. At $\vec{Q}_{\parallel}=0$, symmetry arguments require the surface optical mode either to be nondegenerate and polarized normal to the surface, or doubly degenerate and polarized in the plane of the surface.[17] The fact that the surface-optical-phonon frequency lies very close to the bottom of the LO branch in the (111) direction and close to the top of the LA branch strongly suggests the former to us, but the issue cannot be settled at this time. A detailed study of the surface optical vibrations of a silicon crystal with a (111) surface is under way and will be reported later. At this time, our assumption that the motion is normal to the surface is plausible from the physical point of view, but is still open to question.

Then Eq. (38) becomes

$$|\Delta(Q_{\parallel})|^2 = [16\pi^2 n_0^2 e^2 \epsilon^2/(1+\epsilon)^2] P_{\perp}^2 . \qquad (39)$$

We must now obtain an expression for $\vec{P}_{\perp}$, from a correspondence-principle argument similar to the one used above.

The silicon crystal with a (111) consists of series of layers, each with hexagonal symmetry, for the case where the surface is unreconstructed. Let $(\vec{l}_{\parallel}, l_z)$ be the coordinates of an atom at site $\vec{l}_{\parallel}$ in the layer l_z units from the surface. Then, as above, we write the displacement operator $\vec{u}(\vec{l}_{\parallel} l_z)$ in the form

$$\vec{u}(\vec{l}_{\parallel} l_z) = \sum_{\vec{l}_{\parallel} l_z, n} \frac{\vec{e}_n(\vec{l}_{\parallel} l_z)}{(2M\omega_n)^{1/2}} [a_n + a_n^{\dagger}] ,$$

where, as before, the subscript n denotes the quantum numbers of the mode.

We now construct an expression for the dipole moment associated with the mode. For simplicity, we suppose the surface is unreconstructed. The argument here is easily generalized for any specific model of the reconstructed surface. Upon ignoring surface reconstruction, we can introduce a dipole-moment effective-charge tensor $e^*_{\alpha\beta}(l_z)$, which depends only on l_z. This effective-charge tensor is nonzero only by virtue of the effect of the absence of an inversion center for sites near the surface. Thus, $e^*_{\alpha\beta}(l_z) \to 0$ as one penetrates into the bulk. The change in the electric dipole moment associated with any atom $\vec{P}(\vec{l})$ produced by a displacement $\vec{u}(\vec{l})$ is given by

$$P_{\alpha}(\vec{l}) = \sum_{\beta} e^*_{\alpha\beta}(l_z) u_{\beta}(\vec{l}) .$$

Since a rigid displacement of the crystal cannot produce a change in the dipole moment of the crystal, one requires

$$\sum_{l_z} e^*_{\alpha\beta}(l_z) = 0 .$$

The form $e^*_{\alpha\beta}(l_z)$ can assume is limited by the symmetry of each site. In the crystal with an unreconstructed surface, each site has a threefold axis normal to the surface. The existence of this axis requires $e_{xx}(l_z) = e_{yy}(l_z) \equiv e^*_{\parallel}(l_z)$ and $e_{zz}(l_z) = e^*_{\perp}(l_z)$, with $e_{\alpha\beta}(l_z) = 0$ for $\alpha \neq \beta$. The effective-charge tensor is thus diagonal, with a different effective charge for motion parallel to or normal to the surface.

Then we have

$$P_{\perp}(\vec{l}) = e_{\perp}(l_z) \sum_{n} \frac{\vec{e}_n^{\perp}(l_{\parallel} l_z)}{(2M\omega_n)^{1/2}} [a_n + a_n^{\dagger}] .$$

For the surface optical phonon $\vec{e}_n(l_{\parallel} l_z)$ will have the form

$$\vec{e}_n(\vec{l}_{\parallel} l_z) = (N_s)^{-1/2} e^{iQ_{\parallel} \cdot l_{\parallel}} \vec{\xi}(\vec{Q}_{\parallel}, l_z) .$$

Then, if we consider a single-surface optical phonon of wave vector $\vec{Q}_{\parallel}$, the operator that corresponds to our parameter $P_{\perp}$ is

$$P_{\perp} = \sum_{l_z} \frac{e_{\perp}(l_z)\, \xi_z(\vec{Q}_{\parallel}, l_z)}{[2MN_s\, \omega_s(Q_{\parallel})]^{-1/2}} [a_{Q_{\parallel}} + a^{\dagger}_{-Q_{\parallel}}] .$$

If we consider the case where the electron is scattered, with the absorption of a surface phonon, the correspondence principle dictates replacing $P_{\perp}^2$ with

$$|\langle n_s - 1 | P_{\perp} | n_s \rangle|^2 = \frac{|\sum_{l_z} e_{\perp}(l_z)\, \xi_z(\vec{Q}_{\parallel} l_z)|^2}{2MN_s\, \omega_s(\vec{Q}_{\parallel})} n_s .$$

If the remarks in Sec. II about the character of the surface mode in silicon are recalled, then so long as we consider scattering near the specular direction, where $\vec{Q}_{\parallel}$ is small, we may replace $\vec{Q}_{\parallel}$ by zero in this last result. If we denote the $\vec{Q}_{\parallel} = 0$ surface-optical-mode frequency by ω_s, then we write

$$|\langle n_s - 1 | P_{\perp} | n_s \rangle|^2 = \frac{|q_{\perp}|^2}{2MN_s \omega_s} n_s ,$$

where

$$q_{\perp} = \sum_{l_z} e_{\perp}(l_z)\, \xi_z(o, l_z)$$

is the effective charge of the $\vec{Q}_{\parallel} = 0$ surface optical phonon.

Equation (39) then becomes, for the case where the phonon is absorbed in the scattering processes,

$$|\Delta(Q_{\parallel})|^2 = \frac{8\pi^2 n_0^2 e^2 q_{\perp}^2 \epsilon^2}{MN_s \omega_s (1+\epsilon)^2} n_s \text{ independent of } \vec{Q}_{\parallel}.$$

From Eq. (33), the scattering efficiency per unit solid angle is then (for absorption)

$$\frac{dS}{d\Omega} = \frac{8mn_0 e^2 q_{\perp}^2 \epsilon^2 |R|^2}{M\omega_s E^{(0)} \cos\theta\, (1+\epsilon)^2} n_s \times \frac{(\cos\varphi \cos\theta\psi - \sin\theta\psi_E)^2 + \sin^2\varphi\psi^2}{(\psi^2 + \psi_E^2)^2} , \qquad (40)$$

where we have defined $\psi_E = \hbar\omega_s/2E^{(0)}$.

We first examine some features of Eq. (40) and then we estimate the numerical value of $q_{\perp}$ from Ibach's data. For small values of ψ, we have the solid angle

$$d\Omega = \psi\, d\psi\, d\varphi .$$

We integrate Eq. (40) over φ and thus derive an expression for the total efficiency for scattering into a ring of thickness $d\psi$:

$$\frac{dS}{d\psi} = 8\pi \frac{mn_0 e^2 q_{\perp}^2 \epsilon^2 |R|^2}{M\omega_s E^{(0)} \cos\theta} (1+\cos^2\theta) \frac{\psi(\psi^2 + \gamma^2\psi_E^2)}{(\psi^2 + \psi_E^2)^2} , \qquad (41)$$

where $\gamma^2 = [2\sin^2\theta/(1+\cos^2\theta)]$.

One important difference between the angular distribution for scattering from silicon and from ZnO may be seen from Eq. (41). In both cases, the differential cross section peaks strongly for ψ the order of ψ_E and then falls off to zero for $\psi > \psi_E$. However, for ZnO, when $\psi \gg \psi_E$, $(dS/d\psi)$ varies as ψ^{-2}. The total cross section, obtained by integrating $dS/d\psi$ over all ψ, is perfectly finite, as one can see from Eq. (37). However, for scattering from silicon, for $\psi \gg \psi_E$, $dS/d\psi$ falls off much more slowly with ψ, like ψ^{-1} and not ψ^{-2}. There is for $\psi \gg \psi_E$ a long slowly decaying tail to the angular distribution present in Eq. (41) that is not present in ZnO. When we compute the total observed one-phonon intensity from Eq. (41), we must cut off the result at a cutoff angle ψ_c that is a parameter characteristic of the spectrometer. For $\psi_c \gg \psi_E$, the total intensity S will vary like $\ln(\psi_c/\psi_E)$, while in the case of ZnO, if a cutoff is used, the cross section becomes independent of an angular cutoff, when $\psi_c \gg \psi_E$. We shall also see that for fixed ψ_c, the energy dependence of the one-phonon cross section in silicon is expected to be different for silicon, when compared to the $E^{-1/2}$ dependence characteristic of ZnO.

The difference in the angular distribution and energy dependence of the one-phonon cross section in those two cases is a direct reflection of the distinct character of the surface waves. In ZnO, as $Q_\parallel \to 0$, the thickness of the oscillating electric dipole layer excited by the wave increases as $Q_\parallel^{-1}$. In silicon, the amplitude and thickness of the dipole layer remain fixed. Thus, the study of the energy dependence of the one-phonon cross section should provide a means of distinguishing between the two kinds of surface waves described here.

Upon integrating Eq. (41) from 0, the cutoff value ψ_c, the total efficiency becomes (with $\hbar$ inserted)

$$S = 4\pi \frac{m n_0 e^2 q_\perp^2 \epsilon^2 |R|^2 n_s}{\hbar M \omega_s E^{(0)} \cos\theta} \frac{(1+\cos^2\theta)}{(1+\epsilon)^2} \times \left\{ \frac{(\gamma^2 - 1)\psi_c^2}{\psi_c^2 + \psi_E^2} + \ln\left[1 + \left(\frac{\psi_c}{\psi_E}\right)^2 \right] \right\} . \quad (42)$$

Equation (42) is the scattering efficiency associated with a process in which a phonon is absorbed. The emission cross section may be obtained by replacing n_s by $1 + n_s$.

We now apply this result to silicon. In silicon, $\epsilon = 12$, and $n_0 = 0.8 \times 10^{15}$ unit cells/cm^2. The measurements show $\hbar\omega_s = 55$ meV, and Ibach reports the value of 7×10^{-3} for the ratio of $S/|R|^2$ for electrons of incident energy 5 eV for the emission process. For this incident energy, $\psi_E = 0.32°$, and evidently $\psi_c = 0.5°$ for Ibach's spectrometer.[7] For an angle of incidence of 45°, Eq. (42) gives

$$q_\perp = 0.5 e \quad (43)$$

for the dipole-moment effective charge of the surface mode.

We make some comments about the number displayed in Eq. (43). While there are no microscopic theories of the surface-induced effective charge at this time, we feel this result is a reasonable one. Since $q_\perp$ is nonzero by virtue of the low-site symmetry near the surface and the highly covalent bonds present in silicon can be regarded as rather rigid, we would not expect $q_\perp$ to be large compared to e. If we had ascribed the scattering to modes

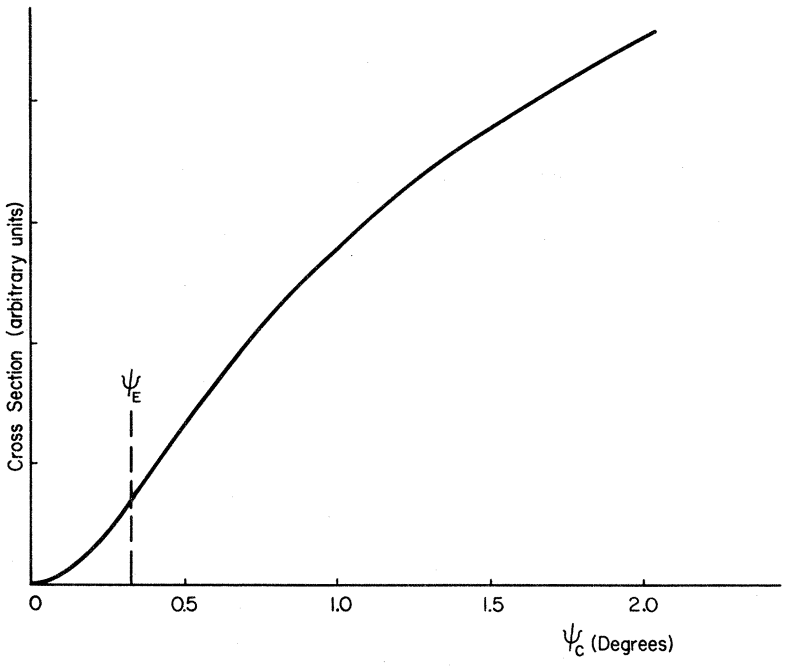

FIG. 3. Dependence of the integrated cross section S on the cutoff angle ψ_c for a circular aperture, for 5-eV electrons incident on the (111) surface of silicon at an angle of 45°.

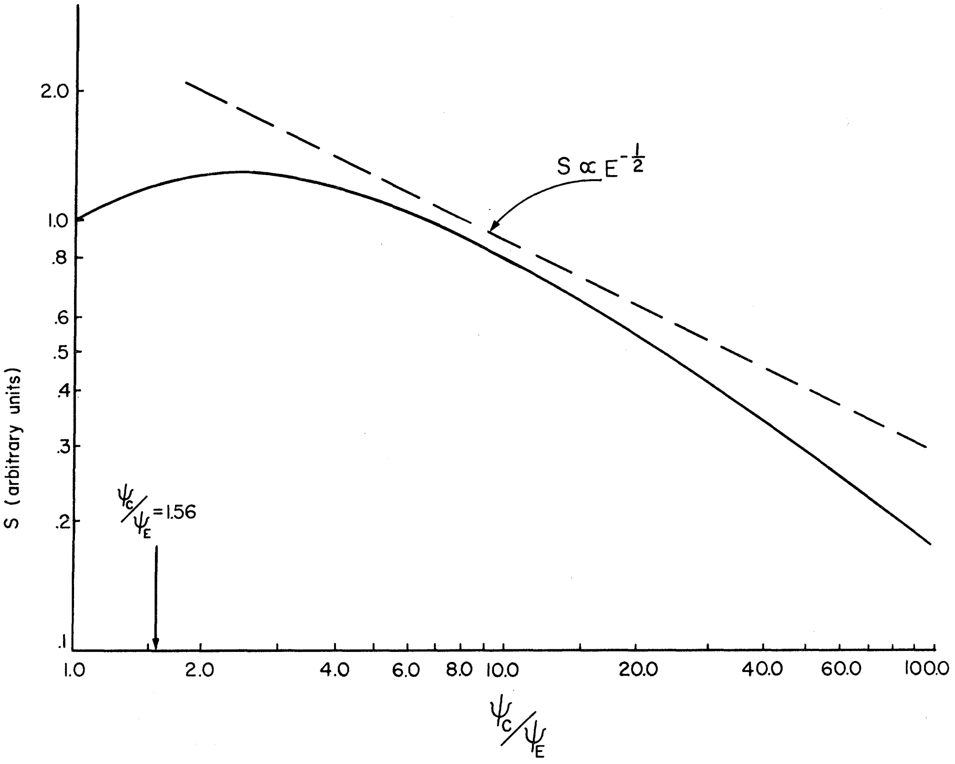

FIG. 4. Energy dependence of the one-phonon cross section. We plot S vs ψ_c/ψ_E for electrons incident on the (111) surface of silicon at an angle of 45°. The dashed line is the result appropriate to the $E^{-1/2}$-law characteristic of the total integrated cross section from ionic crystal, such as ZnO. For 5-eV electrons incident on Si, $\psi_c/\psi_E = 1.56$, as indicated.

polarized parallel to the surface, the effective charge $q_{\parallel}$ for motion parallel to the surface would be larger than the value displayed in Eq. (43) by a factor of ϵ, so $q_{\parallel}$ would have to be the order of $4e$ to explain the observed intensity. If the preceding remark is correct, such a large value of $q_{\parallel}$ would be hard to justify from a physical point of view. We feel this offers further support for our supposition that the scattering is produced by a mode polarized normal to the surface.

In his paper on electron scattering from silicon, Ibach estimated[4] that the effective charge in the surface was the order of $0.1e$, much smaller than our estimate. Since Ibach has not presented the argument he employed to obtain this result, nor defined the effective charge introduced by him, it is difficult to compare our estimate with his.

We conclude by calling attention to Figs. 3 and 4. In Fig. 3, we plot the dependence of the integrated cross section for incident electrons with an energy of 5 eV, as a function of the cutoff angle ψ_c.[18] In Fig. 4, we plot the energy dependence of the one-phonon intensity on a semilog plot. The result is compared to the $E^{-1/2}$ law characteristic of ZnO.[18]

ACKNOWLEDGMENTS

One of us (D. L. M.) is grateful for Dr. H. Ibach for sending us his data on silicon prior to its publication, and to Dr. A. A. Lucas and Dr. Šunjić for a helpful discussion.

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[*] Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, USAF, under Grant No. AFOSR 70-1936. The United States Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation hereon.

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[18] The results in Figs. 3 and 4 are valid only for a circular aperture. For a long slit, such that the narrow part subtends an angle small compared to ψ_E and the large part an angle ψ_c large compared to ψ_E, S would be independent of ψ_c for $\psi_c \gg \psi_E$, and also the total cross section would vary with incident energy roughly as E^{-1}.

PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

Cauchy Relations for Second- and Third-Order Elastic Constants

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(Received 13 January 1972)

The results of an earlier paper on the relation between elastic constants and second- and third-order force constants in face-centered-cubic and body-centered-cubic lattices appeared to conflict with the Cauchy relations $C_{12}=C_{44}$, $C_{112}=C_{166}$, $C_{123}=C_{456}=C_{144}$ obtained by Cousins. We show here that no conflict exists when we ensure that the lattice is in stress-free equilibrium, a necessary condition for Cauchy relations to hold. However, for the case of nearest- and next-nearest-neighbor central-force interactions previously considered, we obtain only special cases of these Cauchy relations. We extend our earlier work to include further neighbors and find that the Cauchy relations are obtained when third neighbors contribute to the elastic constants.

I. INTRODUCTION

In an earlier paper,[1] hereafter referred to as I, on the relation between elastic constants and general second- and third-order force constants in cubic crystals, we also considered the special case of central-force interactions between atoms. The relation between the elastic constants thus obtained, appear to contradict the Cauchy relations for nth-order elastic constants given in a recent paper by Cousins.[2] Cousins shows that the contribution to the elastic constants, $C_{i,j,\ldots}$, from each pair of neighbors is such that all the indices $i, j, \ldots$ may be permuted, not just the Voigt index pairs ij. Thus he obtains the second- and third-order Cauchy relations for cubic crystals,

$$C_{12}=C_{44}\,, \qquad C_{112}=C_{166}\,,$$
$$C_{123}=C_{456}=C_{144}\,. \tag{1}$$

Now the conditions which must be satisfied if the Cauchy relations are to hold are as follows: (i) the atoms must interact with central forces, (ii) every atom must be at a center of inversion, and (iii) the crystal must be free from external stress. Clearly in I, condition (iii) is not satisfied since our expressions for the elastic constants explicitly include a pressure term. Therefore the relations between the elastic constants which we obtained are not the Cauchy relations.

In Sec. II we shall show that when we apply the condition for stress-free equilibrium of a lattice to the relations given in I, our results satisfy a special case of Eq. (1). The general case is obtained when we extend our earlier work to include second- and third-neighbor interactions in the fcc lattice (Sec. III) and bcc lattice (Sec. IV).

In the Appendix, for convenient reference, we quote equations from I that we use in this paper.

II. STRESS-FREE EQUILIBRIUM

The condition for stress-free equilibrium of a lattice with central-force interaction between atoms is given by[3]

$$\sum_l \frac{\partial\psi(r^2)}{\partial r^2}\, x_\alpha x_\beta \Big|_{\vec{x}_l}=0 \qquad (\alpha,\ \beta=1,\ 2,\ 3), \tag{2}$$

where $\psi(r^2)$ is the interatomic potential regarded as a function of the square of the interatomic distance, and $\vec{x}_l$ is the equilibrium position of the lth atom.

For the fcc lattice with nearest-neighbor interactions, Eq. (2) becomes