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Theory of the Inelastic Scattering of Low-Energy Electrons from Crystal Surfaces by One-Phonon Processes*

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In this paper, we present a theoretical discussion of the form of the differential cross section per unit solid angle per unit energy shift for the inelastic scattering by one-phonon processes of low-energy electrons from the surface of a semi-infinite crystal. A number of general features of the cross section are discussed, with particular attention to a comparison with the results obtained from the kinematical theory of the scattering process. We have also carried out a series of numerical studies of the dependence of the shape of the energy-loss spectrum on momentum transfer for an electron incident on the (100) surface of a model fcc crystal. For a general value of the momentum transfer, the energy-loss spectrum consists of one or more lines that arise from the scattering off surface modes, and a band that has its origin in scattering produced by bulk modes. The shape of the latter feature, as well as the position of the surface-mode peaks, is found to be quite sensitive to the values of the atomic force constants appropriate to the surface layer. It is suggested that the experimental study of the shape of the loss spectrum will provide a powerful means of probing the frequency spectrum of the atomic vibrations near the surface.

I. INTRODUCTION

In recent years, a considerable amount of effort has been devoted to the study of the vibrational amplitudes of atoms in crystal surfaces. A number of theoretical approaches to the problem have been developed.[1] Experimentally, one may infer the amplitude of the mean-square displacement in the surface from the temperature dependence of the intensity associated with the elastic scattering of low-energy electrons from the surface. If one utilizes a kinematical description of the scattering process, then the temperature dependence of the low-energy-electron diffraction (LEED) intensity has its origin in the Debye-Waller factors that appear in the expression for the cross section.[2] When the Debye-Waller factors are extracted from the data, one may obtain information about the magnitude of the mean-square displacement in the surface, as well as the anisotropy that results from the lowered site symmetry in the surface layer. Most analyses carried out by this method assume the validity of the kinematical theory. Laramore and Duke[3] have recently completed a detailed analysis of the temperature dependence of the LEED intensity; we refer the reader to their work for a careful discussion of the limits of validity of the kinematical description of the temperature dependence of the LEED intensity.

Even if the kinematical description is a sufficiently accurate one, one obtains information only about the magnitude of the mean-square displacement in the surface layer. It is also of very great interest to study the frequency spectrum of atomic vibrations near the surface. The study of the frequency spectrum will provide a much more severe test of lattice dynamical models of the surface region than the information obtained from the Debye-Waller factors, much in the same way that knowledge of the phonon-dispersion curves of bulk crystals allows a detailed comparison between theory and experiment in a manner not possible on the basis of thermodynamic data alone.

In principle, one may obtain information about the frequency spectrum of atomic vibrations in the surface by studying the inelastic scattering of low-energy electrons. When the electron scatters from the surface, it can gain (lose) energy by the absorption (emission) of phonons. Since the magnitude of the matrix element that describes scattering of the electron by a particular phonon mode clearly depends on the amplitude of the atomic vibrations near the surface associated with the mode, the shape of the loss spectrum provides a probe of the frequency distribution of the atomic vibrations in the surface region. The purpose of this paper is to present a theoretical study of the inelastic scattering of electrons by phonons. We confine our attention to the case where a single phonon is either emitted or absorbed in the scattering process. We present a derivation of the form of the cross section, and we have also completed detailed studies of the dependence of the shape of the energy spectrum on momentum transfer and on the values of the atomic force constants in the surface layer. We find that measurements of the energy-loss spectrum indeed provide a sensitive probe of the vibrational properties of the surface region. The theory presented below does not apply to ionic crystals, where lattice vibrations of long wavelength give rise to spatially extended, macroscopic electric fields outside the crystal.

It will be very difficult to make detailed experimental studies of the energy-loss spectra studied in this work, of course. If the electron loses (gains) energy by emitting (absorbing) a single phonon, then the change in kinetic energy of the particle is only a small fraction of its total energy. The energy change will be the order of 0.05 eV or less. With techniques currently available, it is difficult to obtain electron beams with an energy spread small compared to 0.05 eV. However, two experiments in which energy transfers of this order of magnitude have been detected have been reported recently. Propst and Piper[4] have observed the inelastic scattering of low-energy electrons by hydrogen and by a number of molecular species adsorbed on a tungsten surface. Also, Ibach[5] has observed energy-loss peaks associated with inelastic scattering of low-energy electrons by surface optical phonons in the ionic crystal ZnO. The scattering observed by Ibach arises from the presence of a macroscopic electric field outside the crystal that is associated with surface vibrations of optical character with wavelength long compared to the lattice constant. This scattering is much stronger than the scattering produced by short-wavelength phonons, or by phonons in covalent or metallic crystals. Ibach's measurements are in impressive agreement with the theoretical analysis of Lucas and Sunjic.[6] These long-wavelength surface optical phonons are not sensitive to the properties of the surface layer itself, unfortunately, since the displacements associated with the mode penetrate deeply into the crystal. The experimental work of Propst and Piper and of Ibach demonstrates that detection of energy transfers of the order of magnitude of those considered here is possible, although the experiments are difficult to carry out in practice at the present time.

As mentioned earlier, we are concerned in this work with the inelastic scattering produced by phonons with a wavelength comparable to the lattice constant. The loss spectrum associated with the scattering produced by these modes is quite sensitive to the details of the atomic force constants near the surface, as we shall see. If one examines the energy spectrum of electrons scattered inelastically into a particular solid angle, two features are predicted. A discrete loss peak appears that is produced by scattering from surface waves. In addition, a broad band associated with scattering by *bulk* phonons is present. The integrated intensity of the bulk-phonon band is comparable to the integrated strength of the surface-wave peak in most of the instances examined. The shape of the bulk-phonon band is sensitive to the parameters of the surface region. It should be mentioned at this point that in this paper we are studying the energy spectrum of the electrons that contribute to the thermal diffuse scattering.[7] An estimate of the intensity of the inelastic scattering described below may be obtained by noting that upon integrating our differential cross section for scattering into the solid angle $\Delta\Omega$ with energy transfer between ω and $\omega+\Delta\omega$, over energy transfer ω, one obtains just the contribution to the cross section from one-phonon processes for thermal diffuse scattering into the solid angle $\Delta\Omega$. At high temperatures, this differential cross sections is proportional to the temperature T of the crystal.

In Sec. II, we derive the form for the differential cross section per unit solid angle per unit frequency associated with the inelastic scattering of electrons from the surface by phonon emission or absorption. Some general features of the cross section are also discussed. We have carried out a detailed study of the shape of the loss spectrum, its dependence on momentum transfer and on the atomic force constants of the surface region for a model of a fcc crystal with a free (100) surface. The results of this work, along with a discussion of the general features of the loss spectrum, are presented in Sec. III.

II. FORM OF SCATTERING CROSS SECTION

In this section, we derive the form of the cross section for the scattering of an electron from a semi-infinite crystal for the case where a single quantum of lattice vibration is emitted or absorbed in the process. The derivation fully includes the effect of the static crystal potential on the electronic wave functions; i.e., the electron wave functions of the rigid lattice are supposed to be the Bloch functions appropriate to the semi-infinite geometry. As noted below, there are important *qualitative* differences between the general form we derive in this section and the result of the kinematical description of the inelastic scattering process.[8] In the numerical computations described in Sec. III, we have used an idealization of the general expression. The simplified form employed in Sec. III differs in important qualitative ways from the kinematical result.

We begin by introducing the following Hamiltonian:

$$H = H_E + H_{\text{ph}} + V. \tag{1}$$

In this expression, H_E describes a single electron moving in the effective potential of the crystal lattice, H_{ph} describes the lattice vibrations, and V describes the electron-phonon interaction. We do not explicitly include electron-electron interactions in the Hamiltonian. In the present theory, the effects of electron-electron interactions may be included in a phenomenological fashion by the use of a complex crystal potential in H_E. It will be convenient to employ the specific form

$$H_E = \frac{P^2}{2m} + \sum_{\vec{l}} v_{l_z}(\vec{r} - \vec{R}_{\vec{l}}^{(0)}), \tag{2}$$

where $\vec{r}$ is the position of the electron, $\vec{R}_{\vec{l}}^{(0)}$ is the equilibrium position of the ion at site $\vec{l}$, and $v_{l_z}(\vec{r} - \vec{R}_{\vec{l}}^{(0)})$ is the potential produced by the ion. The surface is in the xy plane, and the subscript l_z allows the potential appropriate to an ion in or near the surface to be different than for an ion in the bulk. The sum over $\vec{l}$ ranges over the semi-infinite lattice. We confine our attention to monatomic crystal lattices and ignore the possibility of surface reconstruction. The eigenstates of H_E have the character of Bloch waves in the x and y direction. We designate the eigenfunctions for an electron in the rigid semi-infinite lattice by the notation $\psi_{\vec{k}_\parallel}^{(\pm)}(\vec{r}_\parallel, z)$, and write

$$\psi_{\vec{k}_\parallel}^{(\pm)}(\vec{r}_\parallel, z) = e^{-i\vec{k}_\parallel \cdot \vec{r}_\parallel}\, U_{\vec{k}_\parallel}^{(\pm)}(\vec{r}_\parallel, z). \tag{3}$$

In Eq. (2), $\vec{r}_\parallel = x\hat{x} + y\hat{y}$ is the projection of the vector to the electron's position onto a plane parallel to surface layer, $\vec{k}_\parallel$ is a wave vector parallel to the surface, and $U_{\vec{k}_\parallel}^{(\pm)}(\vec{r}_\parallel, z)$ is a periodic function of $\vec{r}_\parallel$, i.e.,

$$U_{\vec{k}_\parallel}^{(\pm)}(\vec{r}_\parallel + \vec{t}_\parallel, z) = U_{\vec{k}_\parallel}^{(\pm)}(\vec{r}_\parallel, z),$$

where the semi-infinite lattice is invariant when translated through the displacement $\vec{t}_\parallel$. In general, the subscript $\parallel$ designates vectors which lie in the two-dimensional plane parallel to the surface. Finally, in Eq. (2), the superscript ± designates the outgoing or incoming wave solution of the Schrödinger equation; i.e., $\psi_{\vec{k}_\parallel}^{(+)}$ describes a wave which in the upper half-space (above the crystal) consists entirely of waves that radiate away from the crystal, while $\psi_{\vec{k}_\parallel}^{(-)}$ contains in the upper half-space a single incoming component and a number of outgoing Bragg-reflected waves. The function $\psi_{\vec{k}_\parallel}^{(+)}$ describes transmission through the surface of an electron incident upon the surface from within the crystal, while $\psi_{\vec{k}_\parallel}^{(-)}$ describes reflection from the surface of an electron incident from the vacuum above.

We treat the lattice vibrations in the harmonic approximation, so that (with $\hbar = 1$)

$$H_{\text{ph}} = \sum_n \omega_n a_n^\dagger a_n, \tag{4}$$

where, for the moment, the single quantum index n refers to the nth normal mode of the semi-infinite lattice.

Finally, we write

$$v_{l_z}(\vec{r} - \vec{R}_{\vec{l}}) = \frac{1}{\Omega} \sum_{\vec{q}} v_{l_z}(\vec{q})\, e^{i\vec{q}\cdot(\vec{r} - \vec{R}_{\vec{l}})},$$

where Ω is a quantization volume, and $\vec{R}_{\vec{l}} = \vec{R}_{\vec{l}}^{(0)} + u_{\vec{l}}$ is the instantaneous position of the lth ion, where $u_{\vec{l}}$ is its displacement from the equilibrium position $\vec{R}_{\vec{l}}^{(0)}$. Then

$$V = \frac{1}{\Omega} \sum_{\vec{l}} \sum_{\vec{q}} v_{l_z}(\vec{q})\, e^{i\vec{q}\cdot(\vec{r} - \vec{R}_{\vec{l}}^{(0)})}\, (e^{i\vec{q}\cdot\vec{u}_{\vec{l}}} - 1). \tag{5}$$

Let an electron in the state $|\psi_e\rangle$ be incident on the crystal. The initial state vector of the system has the form $|\psi_0\rangle = |\psi_e\rangle\, |\{n_\alpha\}\rangle$, where $|\{n_\alpha\}\rangle$ describes an eigenstate of H_{ph} in which the αth vibrational mode has n_α phonons excited. The state vector at time t may be obtained by writing the Schrödinger equation in operator form,

$$|\psi(t)\rangle = |\psi_0(t)\rangle - \left(H_E + H_{\text{ph}} - i\frac{\partial}{\partial t}\right)^{-1} V\, |\psi(t)\rangle$$

$$= |\psi_0(t)\rangle + |\delta\psi(t)\rangle . \qquad (6)$$

We calculate the amplitude of the scattered wave $|\delta\psi\rangle$ that is produced by the ionic displacements within the first Born approximation. We thus replace the factor of $|\psi(t)\rangle$ in the expression for $|\delta\psi(t)\rangle$ by the unperturbed wave function $|\psi_0(t)\rangle$:

$$|\delta\psi(t)\rangle = -\left(H_E + H_{\text{ph}} - i\frac{\partial}{\partial t}\right)^{-1} V|\psi_0(t)\rangle . \qquad (7)$$

We shall consider the scattering produced by V into those final states in which a single additional quantum of lattice vibration has been excited. This will then lead us to an expression for the cross section for the scattering of an electron, when it is accompanied by the emission of a single phonon. If E_α is the vibrational energy of the state $|\{n_\alpha\}\rangle$, then upon writing

$$|\psi_0(t)\rangle = e^{-iE_\alpha t}\,|\{n_\alpha\}\rangle|\psi_e(t)\rangle$$

one has

$$|\delta\psi(t)\rangle = -\frac{1}{\Omega}\sum_{\vec{q}\vec{l}} v_{l_z}(\vec{q}) \times \sum_{\{n'_\alpha\}} \frac{|\{n'_\alpha\}\rangle\langle\{n'_\alpha\}|(e^{-i\vec{q}\cdot\vec{u}_{\vec{l}}}-1)|\{n_\alpha\}\rangle}{H_E + E_{\alpha'} - E_\alpha - i\,\partial/\partial t} \times e^{i\vec{q}\cdot(\vec{r}-\vec{R}^{(\alpha)}_{\vec{l}})}|\psi_e(t)\rangle e^{-iE_\alpha t}. \qquad (8)$$

To make the notation compact, let us denote the initial vibrational state of the lattice $|\{n_\alpha\}\rangle$ by $|I_v\rangle$. Consider the matrix element that describes transitions to a state in which the lattice is described by the state vector $|F_v\rangle$. We shall presume that in the state $|F_v\rangle$, the vibrational quantum number n_s of a particular mode s has increased from n_s to n_s+1, with all remaining occupation numbers unchanged. Then

$$E_{\alpha'} - E_{\alpha'} = \omega_s ,$$

where ω_s is the frequency of the phonon created in the scattering process. Then

$$\langle F_v|\delta\psi(t)\rangle = -\frac{1}{\Omega}\sum_{\vec{q},\vec{l}} v_{l_z}(\vec{q})\langle F_v|e^{-i\vec{q}\cdot\vec{u}_{\vec{l}}}|I_v\rangle e^{-iE_\alpha t} \times\left(H_E + \omega_s - i\frac{\partial}{\partial t}\right)^{-1} e^{i\vec{q}\cdot(\vec{r}-\vec{R}^{(0)}_{\vec{l}})}|\psi_e(t)\rangle. \qquad (9)$$

We introduce an electron Green's function $G_s(\vec{r},\vec{r}\,';t-t')$ appropriate to the motion of the electron in the rigid, semi-infinite lattice. Then G_s satisfies

$$\left(H_E + \omega_s - i\frac{\partial}{\partial t}\right) G_s(\vec{r}\vec{r}\,';t-t') = \delta(\vec{r}-\vec{r}\,')\,\delta(t-t').$$

If we write G in Fourier-transformed form, we find

$$G_s(\vec{r}\vec{r}\,';t-t') = \int\frac{dE}{2\pi}\,G(\vec{r}\vec{r}\,';E)\,e^{i(E-\omega_s)(t-t')} ,$$

where $G(\vec{r}\vec{r}\,';E)$ is the solution of

$$(H_E + E)\,G(\vec{r}\vec{r}\,';E) = \delta(\vec{r}-\vec{r}\,') . \qquad (10)$$

We presume $G(\vec{r}\vec{r}\,';E)$ has the boundary conditions appropriate to the present scattering problem appended to it. One may easily show that

$$\left(H_E + \omega_s - i\frac{\partial}{\partial t}\right)^{-1} F(\vec{r},t) = \int d^3\vec{r}\,'dt'\,G_s(\vec{r}\vec{r}\,';t-t')F(\vec{r}\,',t').$$

Thus, upon replacing $|\psi_e(t)\rangle$ in Eq. (9) by the explicit form $\psi_e(\vec{r})e^{-i\mathcal{E}_0 t}$, where $\mathcal{E}_0$ is the initial electron energy, we obtain

$$\langle F_v|\delta\psi(\vec{r},t)\rangle = -\frac{1}{\Omega}\sum_{\vec{q},\vec{l}} v_{l_z}(\vec{q})\langle F_v|e^{-i\vec{q}\cdot\vec{u}_{\vec{l}}}|I_v\rangle e^{-iE_\alpha t} \times\int\frac{dE}{2\pi}\,e^{it(E-\omega_s)}\int d^3r'dt'\,G(\vec{r},\vec{r}\,';E) \times e^{i\vec{q}\cdot(\vec{r}\,'-\vec{R}^{(0)}_{\vec{l}})}\psi_e(\vec{r}\,')e^{-it'(E+\mathcal{E}_0-\omega_s)} . \qquad (11)$$

To proceed, we require the form of the electron Green's function that appears in Eq. (11). Let the symbol n refer to the eigenstate labels for the eigenstates $\psi_n(\vec{r})$ of H_E. Then, if $\mathcal{E}_n$ is the energy of $\psi_n(\vec{r})$, we have

$$G(\vec{r},\vec{r}\,';E) = \sum_n \frac{\psi_n(\vec{r})\psi_n^*(\vec{r}\,')}{E + \mathcal{E}_n + i\eta} . \qquad (12)$$

The zeros of the denominator have been positioned so that $G(\vec{r},\vec{r}\,',t-t')$ vanishes for $t'>t$. Upon inserting Eq. (12) into Eq. (11), the integral over E and over t' may be carried out. One obtains

$$\langle F_v|\delta\psi\rangle = \frac{1}{\Omega}\sum_{\vec{q}\vec{l}} v_{l_z}(\vec{q})\langle F_v|e^{-i\vec{q}\cdot\vec{u}_{\vec{l}}}|I_v\rangle e^{-i\vec{q}\cdot\vec{R}^{(0)}_{\vec{l}}} \times e^{-i(E_\alpha+\mathcal{E}_0+i\eta)t}\sum_n \frac{\langle n|e^{i\vec{q}\cdot\vec{r}}|e\rangle}{\mathcal{E}_n - \mathcal{E}_0 + \omega_s + i\eta}\,\psi_n(\vec{r}). \qquad (13)$$

We define

$$\langle n|e^{i\vec{q}\cdot\vec{r}}|e\rangle = \int d^3r\,\psi_n^*(\vec{r})\,e^{i\vec{q}\cdot\vec{r}}\,\psi_e(\vec{r}) .$$

Let us introduce

$$M^{(s)}(n,e) = \frac{1}{\Omega}\sum_{\vec{q}\vec{l}} v_{l_z}(\vec{q})\langle F_v|e^{-i\vec{q}\cdot\vec{r}_{\vec{l}}}|I_v\rangle e^{-iq\cdot\vec{R}^{(0)}_{\vec{l}}} \times\langle n|e^{i\vec{q}\cdot\vec{r}}|e\rangle . \qquad (14)$$

Then from Eq. (13) it is straightforward to show that the number of transitions per unit time from the initial state ψ_e to the final state ψ_n accompanied by the emission of a phonon of frequency ω_s is given by

$$R_n = 2\pi|M^{(s)}(n,e)|^2\,\delta(\mathcal{E}_n - \mathcal{E}_0 + \omega_s) . \qquad (15)$$

Before the transition rate is converted into an expression for the total differential cross section per unit solid angle per unit frequency, it will be useful to simplify the matrix element in Eq. (14) and also to discuss the kinematics of the scattering process.

First consider the vibrational part $\langle F_v | e^{-i\vec{q}\cdot\vec{u}_{\vec{l}}} | I_v \rangle$ of the matrix element. If p denotes the quantum numbers of a particular normal mode of vibration of the semi-infinite crystal lattice, then

$$\vec{u}_{\vec{l}} = \sum_p \frac{\vec{e}_p(\vec{l})}{(2M\omega_p)^{1/2}} (a_p + a_p^\dagger) . \qquad (16)$$

In Eq. (16), ω_p is the frequency and $\vec{e}_p(\vec{l})$ is the eigenvector of the vibrational mode p, while a_p and $a_p^\dagger$ are the phonon annihilation and creation operators. M is the ionic mass. The eigenvector $\vec{e}_p(\vec{l})$ is normalized so that $\sum_{\vec{l}} |\vec{e}_p(\vec{l})|^2 = 1$.

The state $|I_v\rangle$ is characterized by a well-defined set of phonon-occupation numbers $\{n_\alpha\}$. The set $\{n'_\alpha\}$ associated with the final state $|F_v\rangle$ is the same as the set $\{n_\alpha\}$ save for the occupation number of mode s, which has changed from n_s to $n_s + 1$. The matrix element over the phonon coordinates may then be replaced by

$$\langle F_v | e^{-i\vec{q}\cdot\vec{u}_{\vec{l}}} | I_v \rangle = -i \left(\frac{1 + n(\omega_s)}{2M\omega_s} \right)^{1/2} \vec{q} \cdot \vec{e}_s(\vec{l}) \times \exp[-\tfrac{1}{2} \langle (\vec{q} \cdot \vec{u}_{\vec{l}})^2 \rangle_T] , \qquad (17)$$

where $n(\omega_s) = (e^{\beta\omega_s} - 1)^{-1}$ is the Bose-Einstein factor, β is $1/kT$, and $\langle (\vec{q} \cdot \vec{u}_{\vec{l}})^2 \rangle_T$ is the thermal average of $(\vec{q} \cdot \vec{u}_l)^2$. Note that $\langle (\vec{q} \cdot \vec{u}_{\vec{l}})^2 \rangle_T$ is a function only of l_z. It is then useful to introduce a renormalized effective potential $\tilde{v}$, with a Fourier transform given by

$$\tilde{v}_{l_z}(\vec{q}) = v_{l_z}(\vec{q}) \exp[-\tfrac{1}{2} \langle (\vec{q} \cdot \vec{u}_{\vec{l}})^2 \rangle_T] .$$

Then Eq. (14) becomes

$$M^{(s)}(n, e) = -\frac{i}{\Omega} \sum_{\vec{q}\vec{l}} \tilde{v}_{l_z}(\vec{q}) \left(\frac{1 + n(\omega_s)}{2M\omega_s} \right)^{1/2} \times \vec{q} \cdot \vec{e}_s(\vec{l}) e^{-i\vec{q}\cdot\vec{R}_{\vec{l}}^{(0)}} \langle n | e^{i\vec{q}\cdot\vec{r}} | e \rangle .$$

Next consider the matrix element over the electronic coordinate $\vec{r}$. The incident state $\psi_e(\vec{r})$ is a Bloch function of the form

$$\psi^{(-)}_{\vec{k}_\parallel{}^{(0)}, \mathcal{E}_0} (\vec{r}_\parallel, z) = e^{-i\vec{k}_\parallel{}^{(0)}\cdot\vec{r}_\parallel} U^{(-)}_{\vec{k}_\parallel^{(0)}, \mathcal{E}_0} (\vec{r}_\parallel, z) .$$

The superscript (–) indicates a Bloch function that describes an electron incident on the crystal from above, as described earlier in this section. We presume $\psi^{(-)}_{\vec{k}_\parallel^{(0)}, \mathcal{E}_0}$ is normalized so that in the region $z > 0$, the single incoming component is proportional to $e^{i\vec{k}^{(0)}\cdot\vec{r}}$, where $\vec{k}^{(0)}$ is the wave vector of the incoming electron. Once $\vec{k}_\parallel^{(0)}$ and the energy $\mathcal{E}_0$ of the incoming electron is specified, then $\psi^{(-)}_{\vec{k}_\parallel^{(0)}, \mathcal{E}_0}$ is uniquely specified. For the outgoing state $\psi_n(\vec{r})$, we require the function $\psi^{(+)}_{\vec{k}_\parallel^{(s)}, \mathcal{E}_s}$; this choice is dictated by the boundary condition imposed on the Green's function $G(\vec{r}, \vec{r}\,'; t - t')$. For simplicity, we assume the outgoing state is completely specified by the two quantities $\vec{k}_\parallel^{(s)}$ and $\mathcal{E}_s$, although there may be cases where additional quantum numbers may be required to specify the outgoing state. We also use the reduced zone scheme to label the wave vectors, i.e., both $\vec{k}_\parallel^{(0)}$ and $\vec{k}_\parallel^{(s)}$ lie in the first Brillouin zone of the two-dimensional reciprocal lattice appropriate to the surface layer. One then finds that

$$\begin{aligned} \langle n | e^{i\vec{q}\cdot\vec{r}} | e \rangle &\equiv \langle \vec{k}_\parallel^{(s)}, \mathcal{E}_s | e^{i\vec{q}\cdot\vec{r}} | \vec{k}_\parallel^{(0)}, \mathcal{E}_0 \rangle \\ &= A_c N_s \delta_{\vec{k}_\parallel{}^{(s)}, \vec{k}_\parallel^{(0)} - \vec{q}_\parallel + \vec{G}_\parallel} \langle\langle \vec{k}_\parallel^{(s)}, \mathcal{E}_s | e^{iq_z z} e^{i\vec{G}_\parallel\cdot\vec{r}_\parallel} | \vec{k}_\parallel^{(0)}, \mathcal{E}_0 \rangle\rangle . \end{aligned}$$

In this expression, N_s is the number of atoms in the surface layer of the crystal, A_c the area of a unit cell, and $\delta_{\vec{q},\vec{q}\,'} = 1$ if $\vec{q} = \vec{q}\,'$, and vanishes otherwise. If $\vec{k}_\parallel^{(0)} - \vec{q}_\parallel$ lies in the first Brillouin zone associated with the surface layer, then $\vec{G}_\parallel = 0$. Otherwise $\vec{G}_\parallel$ is that (unique) reciprocal lattice vector which places $\vec{k}_\parallel^{(0)} - \vec{q}_\parallel + \vec{G}_\parallel$ in the first zone. Finally we define

$$\langle\langle \vec{k}_\parallel^{(s)}, \mathcal{E}_s | e^{i\vec{k}\cdot\vec{r}} | \vec{k}_\parallel^{(0)}, \mathcal{E}_0 \rangle\rangle = \int_{\text{one unit cell}} \frac{d^2\vec{r}_\parallel}{A_c} \int_{-\infty}^{0} dz \times U^{(+)*}_{\vec{k}_\parallel(s), \mathcal{E}_s} (\vec{r}_\parallel, z) \, e^{i\vec{k}\cdot\vec{r}} U^{(-)}_{\vec{k}_\parallel(0), \mathcal{E}_0} (\vec{r}_\parallel, z) .$$

The integral over $\vec{r}_\parallel$ is confined to that unit cell of the surface layer which contains the origin of the coordinate system, and the integral over z is confined to the region $z < 0$, since the scattering potential vanishes for $z > 0$. Upon writing the quantization volume $\Omega = N_s A_c L$, Eq. (14) becomes

$$\begin{aligned} M^{(s)}(\vec{k}_\parallel^{(s)} \mathcal{E}_s, \vec{k}_\parallel^{(0)} \mathcal{E}_0) &= -\frac{i}{L} \left(\frac{1 + n(\omega_s)}{2M\omega_s} \right)^{1/2} \sum_{q_z \vec{l}} \tilde{v}_{l_z}(\vec{K}) [\vec{K} \cdot \vec{e}_s(\vec{l})] e^{-i\vec{K}\cdot\vec{R}_{\vec{l}}^{(0)}} \\ &\quad \times \langle\langle \vec{k}_\parallel^{(s)}, \mathcal{E}_s | e^{iq_z z} e^{i\vec{G}_\parallel\cdot\vec{r}_\parallel} | \vec{k}_\parallel^{(0)}, \mathcal{E}_0 \rangle\rangle . \qquad (18) \end{aligned}$$

The vector $\vec{K}$ has the components

$$\vec{K}_\parallel = \vec{k}_\parallel^{(0)} - \vec{k}_\parallel^{(s)} + \vec{G}_\parallel , \qquad K_z = q_z .$$

We proceed further in the reduction process by noting the nature of the normal modes of vibration of the semi-infinite crystal. Since formation of the surface does not destroy the translational invariance of the crystal in the two dimensions parallel to the surface (recall that we ignore the possibility of surface reconstruction in this work), the normal modes of vibration have the character of plane waves as far as the two directions normal to the surface are concerned. Thus, we write

$$\vec{e}_s(\vec{l}) = \frac{1}{(N_s)^{1/2}} \sum_{\vec{k}_\parallel^{(p)}, \alpha} \vec{e}_{\vec{k}_\parallel^{(p)}, \alpha} (l_z) \, e^{-i\vec{k}_\parallel^{(p)}\cdot\vec{l}_\parallel} , \qquad (19)$$

where the index s of the phonon mode is replaced by the set $\vec{k}_{\parallel}^{(p)}$, α. The index α labels the particular mode with wave vector $\vec{k}_{\parallel}^{(p)}$ parallel to the surface under consideration; α may refer to either a bulk wave or a surface (Rayleigh) wave. Upon inserting Eq. (19) into Eq. (18), the sum over $\vec{l}_{\parallel}$ may be carried out. Upon introducing a more explicit notation for the matrix element, we find

$$M^{(s)}(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)\equiv M(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0;\vec{k}_{\parallel}^{(p)}\alpha),$$

where

$$\begin{aligned}M(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0;\vec{k}_{\parallel}^{(p)}\alpha)&\\ =-\frac{i}{L}\left(\frac{N_s}{2M\omega_{\vec{k}_{\parallel}^{(p)},\alpha}}\right)^{1/2}&[1+n(\omega_{\vec{k}_{\parallel}^{(p)},\alpha})]^{1/2}\,\delta_{\vec{k}_{\parallel},\vec{k}_{\parallel}^{(p)}}\\ \times\sum_{q_z l_z}\tilde{v}_{l_z}(\vec{K})[\vec{K}\cdot\vec{e}_{\vec{k}_{\parallel}^{(p)},\alpha}(l_z)]e^{-iq_z l_z}&\\ \times\langle\langle\vec{k}_{\parallel}^{(s)},\mathcal{E}_s|e^{iq_z z}e^{i\vec{G}_{\parallel}\cdot\vec{r}_{\parallel}}|\vec{k}_{\parallel}^{(0)},\mathcal{E}_0\rangle\rangle\,.&\qquad(20)\end{aligned}$$

It will be convenient to write Eq. (20) in a more compact form. Define

$$\begin{aligned}m_{l_z}(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)&=\frac{i}{L}\sum_{q_z}\tilde{v}_{l_z}(\vec{K})\,e^{-iq_z l_z}\\ &\times\langle\langle\vec{k}_{\parallel}^{(s)},\mathcal{E}_s|e^{iq_z z}\,e^{i\vec{G}_{\parallel}\cdot\vec{r}_{\parallel}}|\vec{k}_{\parallel}^{(0)},\mathcal{E}_0\rangle\rangle\,,\\ Q_z(l_z)&=\frac{i}{m_{l_z}(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s,\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)\,L}\sum_{q_z}q_z\tilde{v}_{l_z}(K)\,e^{-iq_z l_z}\\ &\times\langle\langle\vec{k}_{\parallel}^{(s)},\mathcal{E}_s|e^{iq_z z}e^{i\vec{G}_{\parallel}\cdot\vec{r}_{\parallel}}|\vec{k}_{\parallel}^{(0)},\mathcal{E}_0\rangle\rangle\\ &\equiv\frac{i}{m_{l_z}(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)}\,\frac{\partial m_{l_z}(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)}{\partial l_z}\,.\end{aligned}\tag{21}$$

Then, finally let the vector $\vec{Q}$ have the form

$$\vec{Q}=\vec{k}_{\parallel}^{(p)}+\hat{z}\;Q_z(l_z)\,.\tag{22}$$

With these definitions, Eq. (20) becomes

$$\begin{aligned}M(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0;\vec{k}_{\parallel}^{(p)}\alpha)&\\ =-(N_s/2M\omega_{\vec{k}_{\parallel}^{(p)},\alpha})^{1/2}&\,[1+n(\omega_{\vec{k}_{\parallel}^{(p)},\alpha})]^{1/2}\,\delta_{\vec{k}_{\parallel}^{(p)}}\\ \times\textstyle\sum_{l_z}[\vec{Q}'\,\vec{e}_{\vec{k}_{\parallel}^{(p)},\alpha}(l_z)]&\,m_{l_z}(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)\,.\end{aligned}\tag{23}$$

We could now proceed to discuss the kinematics of the scattering process, and then to construct an expression for the appropriate differential cross section from the transition rate displayed in Eq. (15). However, we prefer to first point out an important feature of the matrix element displayed in Eq. (23).

We wish to consider the relationship between the matrix element displayed in Eq. (23) and the kinematical description of the inelastic scattering process. A matrix element equivalent to that obtained from the kinematical theory may be obtained from Eq. (23) only by presuming the wave function of the electron to be plane-wave-like (and unattenuated) in the z direction. More specifically, suppose that in the crystal $U_{\vec{k}_{\parallel},\mathcal{E}}(\vec{r}_{\parallel},z)$ is well approximated by the form

$$U_{\vec{k},\mathcal{E}}(\vec{r}_{\parallel},z)=e^{-ik_z z}f_{\vec{k}_{\parallel},\mathcal{E}}(\vec{r}_{\parallel})\,.$$

Then it follows that

$$\begin{aligned}\langle\langle\vec{k}_{\parallel}^{(s)},\mathcal{E}_s|e^{iq_z z}|\vec{k}_{\parallel}^{(0)},\mathcal{E}_0\rangle\rangle&\\ =LI(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)\,\delta_{q_z,k_z^{(0)}-k_z^{(s)}}\,,&\end{aligned}\tag{24}$$

where $I(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)$ is independent of q_z. Introduce the vector

$$\vec{\Delta}=\vec{k}_{\parallel}^{(0)}-\vec{k}_{\parallel}^{(s)}+\vec{G}_{\parallel}+\hat{z}(k_z^{(0)}-k_z^{(s)})\;.$$

Then from Eq. (24), one has

$$m_{l_z}(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)=i\tilde{v}_{l_z}(\vec{\Delta})I(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)e^{il_z\Delta_z}\,,$$

and

$$Q_z=k_z^{(0)}-k_z^{(s)}=\Delta_z$$

independent of l_z. Thus, we may replace $\vec{Q}$ by $\vec{\Delta}$, in this approximation. The matrix element in Eq. (23) then assumes the form

$$\begin{aligned}M(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0;\vec{k}_{\parallel}^{(p)}\alpha)=-\delta_{\vec{k}_{\parallel}^{(p)},\vec{K}_{\parallel}}&I(\vec{k}_{\parallel}^{(s)}\mathcal{E}_s;\vec{k}_{\parallel}^{(0)}\mathcal{E}_0)\\ \times\sum_{l_z}\tilde{v}_{l_z}(\vec{\Delta})e^{il_z\Delta_z}&[\vec{\Delta}\cdot\vec{e}_{\vec{k}_{\parallel}^{(p)},\alpha}(l_z)]\\ \times(N_s/2M\omega_{\vec{k}_{\parallel}^{(p)},\alpha})^{1/2}&[1+n(\omega_{\vec{k}_{\parallel}^{(p)},\alpha})]^{1/2}\,.\end{aligned}\tag{25}$$

The result displayed in Eq. (25) is equivalent to the result obtained from a kinematical description of the scattering process,[8] for all practical purposes. The assumption required to obtain the form of Eq. (25) is a very severe one, unfortunately. There are three fundamental reasons why the assumption about the form of the wave function in the crystal will provide a very poor approximation to the true wave function. First of all, the crystal potential produces strong distortions of the wave functions away from the plane-wave form. This is particularly true in the transition metals, where the wave functions have strong d character. Secondly, because of the presence of the surface, the wave function in the solid will consist of an admixture of infinite-crystal Bloch waves, in order for the wave function to match properly to the plane waves in the vacuum outside the metal. For example, $\psi_{\vec{k}_{\parallel}}^{(+)}$ will contain a wave incident on the surface from below (from within) the crystal, as well as reflected waves. Finally, the electron wave is very strongly attenuated as it penetrates into the crystal, because of electron-electron interactions. To properly compute the matrix element, one should employ an optical potential, or a potential with a complex part. Thus, even if the periodic part of the crystal potential is well approximated by a weak perturbation, the incoming and scattered beam are strongly attenuated in the medium, and the wave functions will be best approximated by strongly attenuated plane waves. Duke and Tucker[9] have demonstrated that it is absolutely essential to include this feature of the propagation of the electron in the crystal before one can make contact with LEED data. The mean free path of electrons in the crystal is, in fact, comparable in magnitude to the de Broglie wavelength for energies typically encountered in LEED experiments.

Thus, we expect in general that the kinematical theory will provide a very poor description of the matrix element that describes the inelastic scattering of low-energy electrons by lattice vibrations. It remains to examine the general form of Eq. (23) to see what features of the kinematical description remain. First, consider the contribution to M from ionic motion parallel to the surface. This portion of M (we call it $M_\parallel$ for convenience) is obtained from Eq. (23) by retaining only the components of the eigenvector $\vec{e}_{\vec{k}_\parallel^{(p)},\alpha}(l_z)$ parallel to the surface. One can see that since

$$\vec{K}_\parallel = \vec{k}_\parallel^{(p)} = \vec{k}_\parallel^{(0)} - \vec{k}_\parallel^{(s)} - \vec{G}_\parallel ,$$

$M_\parallel$ can be written in a from quite similar to the analogous portion of the right-hand side of Eq. (25) provided the scattering amplitude associated with each plane [the factor $\tilde{v}_{l_z}(\vec{\Delta})e^{il_z\Delta_z}$ in Eq. (25)] is replaced by a more complicated quantity. Thus, the contribution from lattice motion parallel to the surface to those properties of the inelastic scattering that are not sensitive to the precise form of this scattering amplitude are correctly described by the kinematical theory, provided one regards the planar scattering strengths as phenomenological parameters. For example, we expect the contribution from lattice motions parallel to the surface to the dependence of the intensity of the thermal diffuse scattering on scattering angle[8] to be correctly given by the kinematical theory. The matrix element for scattering produced by lattice motion *normal* to the surface (call the contribution from this motion to the matrix element $M_\perp$) that results from the kinematical theory is seriously in error, however. In general, the parameter Q_z on the right-hand side of Eq. (23) depends on all the parameters of the scattering geometry ($\vec{k}_\parallel^{(s)}$, $\mathcal{E}_s$; $\vec{k}_\parallel^{(0)}$, $\mathcal{E}_0$) as well as l_z, as one can see from its definition. It is not related to the parameter $k_z^{(0)} - k_z^{(s)}$ of the kinematical theory in any simple fashion. Thus, in contrast to the situation with $M_\parallel$, $M_\perp$ cannot be written in a form that differs from the kinematical expression only by virtue of a more sophisticated expression for the planar scattering amplitude. This difficulty will make difficult the detailed analysis of the energy-loss spectrum of low-energy electrons that results from phonon scattering. However, we shall see that one can still obtain a large amount of information from qualitative features of the spectrum.

We now proceed to obtain the form of the differential cross section for the inelastic scattering of electrons by emission of a single quantum of lattice vibration. First, some remarks about the kinematics of the scattering process will be useful. The discussion we present here is very similar to an earlier description by Mills, Maradudin, and Burstein[10] of the inelastic scattering of photons by optical phonons in opaque crystals.

The incident electron has energy $\mathcal{E}_0$ and wave-vector component $\vec{k}_\parallel^{(0)}$ parallel to the surface. The direction of the incoming beam may be determined by noting that

$$k_z^{(0)} = -[2m\mathcal{E}_0 - (\vec{k}_\parallel^{(0)})^2]^{1/2}.$$

Let the electron strike the crystal and scatter from it by a process that involves emission of a phonon of frequency $\omega_{\vec{k}_\parallel^{(p)},\alpha}$ with wave-vector component $\vec{k}_\parallel^{(p)}$ parallel to the surface. The electron is scattered into the state $\psi^{+}_{\vec{k}_\parallel^{(s)}}$, where

$$\vec{k}_\parallel^{(s)} = \vec{k}_\parallel^{(0)} - \vec{k}_\parallel^{(p)} + \vec{G}_\parallel ,$$

as we have seen. The outgoing electron thus has energy

$$\mathcal{E}_s = \mathcal{E}_0 - \omega_{\vec{k}_\parallel^{(p)},\alpha} . \tag{26}$$

The state $\psi^{(+)}$ can contain more than one outgoing current; in general, outside the metal, it consists of a linear conbination of all possible plane waves with energy $\mathcal{E}_s$ and wave vectors $\vec{k}_\parallel^{(s)} + \vec{g}_\parallel$ parallel to the surface, where $\vec{g}_\parallel$ is any reciprocal lattice vector associated with the crystal surface. A plane wave characterized by any reciprocal lattice vector $\vec{g}_\parallel$ such that

$$\mathcal{E}_s - (1/2m)\,(\vec{k}_\parallel^{(s)} + \vec{g}_\parallel)^2 > 0$$

can occur in the propagating part of the outgoing wave, provided it is allowed by the boundary conditions to mix in the wave function.

Consider an outgoing wave characterized by some particular $\vec{g}_\parallel$. Given $\vec{k}_\parallel^{(p)}$, the frequency $\omega_{\vec{k}_\parallel^{(p)},\alpha}$ of the particular phonon involved in the scattering process, and the incident scattering geometry, the direction of the outgoing wave is determined by Eq. (26) combined with the statement of conservation of total wave vector parallel to the surface,

$$\vec{k}_\parallel^{(s)} = \vec{k}_\parallel^{(0)} - \vec{k}_\parallel^{(p)} + \vec{G}_\parallel , \tag{27}$$

and the statement that

$$k_z^{(s)}(\vec{g}_\parallel) = [2m\mathcal{E}_s - (\vec{k}_\parallel^{(s)} + \vec{g}_\parallel)^2]^{1/2} . \tag{28}$$

Consider the relative order of magnitude of the quantities that appear in Eqs. (26)–(28). In general, under conditions appropriate to standard LEED experiments, one finds that $\vec{k}^{(0)}$, $\vec{k}^{(s)}$, $\vec{G}_\parallel$, and $\vec{g}_\parallel$ are all the same order of magnitude, since the de Broglie wavelength of the incident and scattered electron are comparable to the lattice constant. Similarly, we shall look at scatterings for which the phonon wavelength is comparable to the lattice constant. However, $\omega_{\vec{k}_\parallel^{(p)},\alpha} \ll \mathcal{E}_0$ and $\mathcal{E}_s$. Thus little error results if the phonon frequency that appears in Eq. (26) is ignored. When this is done, the direction of the outgoing electron depends sensitively on the wave-vector component $\vec{k}_\parallel^{(p)}$ of the phonon parallel to the surface, but not on its frequency. Thus, a Rayleigh wave and a bulk phonon will both scatter the electron into the same solid angle $\Delta\Omega$, provided they are both characterized by the same wave-vector component $\vec{k}_\parallel^{(p)}$ parallel to the surface. This feature of the kinematics of the scattering process will greatly simplify our subsequent analysis. Also, it should make interpretation of data relatively straightforward, since one can associate the loss spectrum associated with electrons scattered into a given solid angle $\Delta\Omega$ with an easily visualized portion of the lattice-vibration spectrum of a solid.

In Fig. 1, we present a sketch of the vibrational spectrum of a semi-infinite solid in a form suitable for a discussion of the loss spectrum associated with one-phonon processes. The figure illustrates, for each value of $\vec{k}_\parallel$, the bands of vibrational frequency allowed for the solid. The sketch is presented for the purposes of illustration only, and in any specific situation the details may differ substantially from this figure. In the figure, for each value of $\vec{k}_\parallel$ one has a Rayleigh surface wave. In addition, a band of bulk vibrations ranging between a minimum frequency $\omega_{\min}$ and a maximum frequency $\omega_{\max}$ occurs. In a typical case, speaking somewhat loosely, a phonon propagating parallel to the surface with wave vector $\vec{k}_\parallel$ may have the frequency $\omega_{\min}$, while $\omega_{\max}$ may be associated with a phonon moving more nearly normal to the surface, with a large value of k_z and wave-vector component $\vec{k}_\parallel$ in the plane parallel to the surface. As stated earlier, all modes with the same value of $\vec{k}_\parallel$ scatter electrons into the same solid angle. Thus, all the modes that lie on the vertical line in Fig. 1 scatter into the same outgoing direction. Examination of the shape of the loss spectrum associated with this outgoing direction will thus show a discrete loss peak associated with scattering off surface waves, and a broad band that ranges from $\omega_{\min}$ to $\omega_{\max}$ produced by scattering from bulk phonons. The shape of the broad band is sensitive to the parameters that describe the lattice-dynamical properties of the surface region, as we shall see. Of course, the frequency of the surface wave and intensity of the scattering from this mode are also dependent on these parameters.

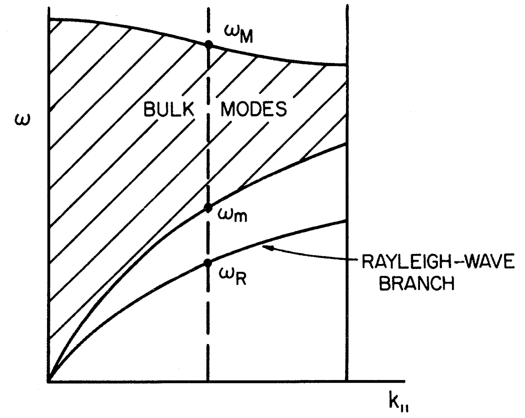

FIG. 1. Sketch of the phonon spectrum of a monatomic semi-infinite lattice. Associated with a given wave-vector component $k_\parallel$ parallel to the surface, one has a Rayleigh surface wave as well as a band of continuum modes. All modes with the same value of $k_\parallel$ scatter an incident low-energy electron in the same outgoing direction, to a good approximation.

The crucial feature of the argument just presented is the observation that $\mathcal{E}_0$, $\mathcal{E}_s \gg \omega_{\vec{k}_\parallel^{(p)},\alpha}$. Thus, if one observes inelastic scattering of slow atoms by one-phonon processes from the surface, then $\mathcal{E}_0$, $\mathcal{E}_s$, and the phonon frequencies are comparable. The atoms scattered into a given solid angle $\Delta\Omega$ will have scattered from modes that lie on a curved trajectory in the plane of Fig. 1. Since the shape of this trajectory depends on the details of the phonon spectrum, it may be less straightforward to associate features in the energy-loss spectrum of slow atoms with well-defined features in the vibrational spectrum of solid.

With these remarks in mind, we now obtain an expression for the differential cross section per unit solid angle per unit frequency for the inelastic scattering of low-energy electrons from the surface. We begin with Eq. (15), which we write in the more explicit form

$$R(\vec{k}_\parallel^{(0)}\mathcal{E}_0 \to \vec{k}_\parallel^{(s)}\mathcal{E}_s) = 2\pi \left| M(\vec{k}_\parallel^{(0)}\mathcal{E}_0,\, \vec{k}_\parallel^{(s)}\mathcal{E}_s;\, \vec{k}_\parallel^{(p)}\alpha)\right|^2 \times \delta(\mathcal{E}_s - \mathcal{E}_0 + \omega_{\vec{k}_\parallel^{(p)},\alpha}) .$$

This is the transition rate into the single final state $(\vec{k}_\parallel^s,\ \mathcal{E}_s)$ produced by the single mode $\vec{k}_\parallel^{(p)}\alpha$. First we calculate the total outgoing current. Outside the crystal, the state $\psi^{(+)}_{\vec{k}_\parallel^{(s)}}$ has the form

$$\psi^{(+)}_{\vec{k}_\parallel^{(s)}}(\vec{r}_\parallel, z) = (\Omega)^{-1/2} \sum_{\vec{g}_\parallel} e^{i(\vec{k}_\parallel^{(s)} + \vec{g}_\parallel)\cdot\vec{r}_\parallel} e^{ik_z(\vec{g}_\parallel)z} a_{\vec{k}_\parallel^{(s)}}(\vec{g}_\parallel) ,$$

where

$$k_z(\vec{g}_\parallel) = [2m\mathcal{E}_s - (\vec{k}_\parallel^{(s)} + \vec{g}_\parallel)^2]^{1/2} .$$

When the argument of the square root is negative, $k_z(\vec{g}_\parallel)$ is chosen to have a positive imaginary part. The outgoing wave into which the electron is scattered thus consists in the general case of more than one outgoing beam. If $v^{(s)}$ is the group velocity of an electron with energy $\mathcal{E}_s$ in free space, the current $\delta j^{(s)}(\vec{k}_\parallel^{(s)} + \vec{g}_\parallel)$ carried by the outward wave propagating in the direction $\vec{k}_\parallel^{(s)} + \vec{g}_\parallel + \hat{z}k_z(\vec{g}_\parallel)$ is given by

$$\delta j^{(s)}(\vec{k}_\parallel^{(s)} + \vec{g}_\parallel) = (2\pi v^{(s)}/\Omega)\,|a_{\vec{k}_\parallel^{(s)}}(\vec{g}_\parallel)|^2 |M(\cdots)|^2 \times \delta(\mathcal{E}_s - \mathcal{E}_0 + \omega_{\vec{k}_\parallel^{(p)},\alpha}) .$$

This expression gives the contribution to the outgoing current that obtains from scattering into the single final state $(\vec{k}_\parallel^{(s)}, \mathcal{E}_s)$. To find the total outgoing current produced by scattering off the single mode $(\vec{k}_\parallel^{(p)}, \alpha)$, one sums this result over the values of the wave vector of the final electron state. Upon noting the factor of $\delta_{\vec{k}_\parallel, \vec{k}_\parallel^{(p)}}$ that appears in the matrix element [see Eq. (20)], we obtain

$$\begin{aligned}\delta j^{(s)} &= \sum_{\vec{k}_\parallel^{(s)}} \sum_{k_z(\vec{g}_\parallel)} \delta j^{(s)}(\vec{k}_\parallel^{(s)} + \vec{g}_\parallel) \\ &= \frac{2\pi v^{(s)}}{\Omega} \frac{L}{2\pi} \int dk_z |a_{\vec{k}_\parallel^{(s)}}(\vec{g}_\parallel)|^2 |M(\cdots)|^2 \\ &\qquad \times \delta(\mathcal{E}_s - \mathcal{E}_0 + \omega_{\vec{k}_\parallel^{(p)},\alpha}) \\ &= \frac{v^{(s)}}{Av_z^{(s)}(\vec{g}_\parallel)} |a_{\vec{k}_\parallel^{(s)}}(\vec{g}_\parallel)|^2 \, |M(\vec{k}_\parallel^{(0)}\mathcal{E}_0, \vec{k}_\parallel^{(s)}\mathcal{E}_s, \vec{k}_\parallel^{(p)}\alpha)|^2 .\end{aligned}$$

We have taken the quantization volume Ω to have area A (the area of the crystal) and length L. The quantity $v_z^{(s)}(\vec{g}_\parallel)$ is the z component of the group velocity of the outgoing electron wave in the direction $\vec{k}_\parallel^{(s)} + \vec{g}_\parallel + \hat{z}k_z(\vec{g}_\parallel)$.

All phonons with the same value of $\vec{k}_\parallel^{(p)}$ scatter electrons into the same outgoing direction to a very good approximation, as we have seen. Let the number of phonon modes with frequency between ω and $\omega + \Delta\omega$ and with wave-vector component $\vec{k}_\parallel^{(p)}$ parallel to the surface be $\rho(\vec{k}_\parallel^{(p)}, \omega)\Delta\omega$. Then the contribution to the current in the outgoing direction from those electrons which suffer an energy shift $\mathcal{E}_0 - \mathcal{E}_s$ between $\omega_{\vec{k}_\parallel^{(p)},\alpha}$ and $\omega_{\vec{k}_\parallel^{(p)},\alpha} + \Delta\omega$ is given by

$$\delta J^{(s)} = \frac{v^{(s)}}{Av_z^{(s)}(\vec{g}_\parallel)} \, |a_{\vec{k}_\parallel^{(s)}}(\vec{g}_\parallel)|^2 \, |M(\vec{k}_\parallel^{(0)}\mathcal{E}_0, \vec{k}_\parallel^{(s)}\mathcal{E}_s, \vec{k}_\parallel^{(p)}\alpha)|^2 \times \rho(\vec{k}_\parallel^{(p)}, \omega_{\vec{k}_\parallel^{(p)},\alpha})\Delta\omega . \quad (29)$$

Consider the total scattering produced by all the modes in the frequency range $\omega_{\vec{k}_\parallel^{(p)},\alpha}$, $\omega_{\vec{k}_\parallel^{(p)},\alpha} + \Delta\omega$, and with wave-vector component in the area $d^2\vec{k}_\parallel^{(p)}$ of the first Brillouin zone of the $\vec{k}_\parallel^{(p)}$ plane centered about the value $\vec{k}_\parallel^{p}$ that appears in Eq. (29). Suppose these modes scatter the electrons into the solid angle $\Delta\Omega$. Then the total number of electrons that suffer an energy shift between $\omega_{\vec{k}_\parallel^{(p)},\alpha}$ and $\omega_{\vec{k}_\parallel^{(p)},\alpha} + \Delta\omega$, while being scattered into solid angle $\Delta\Omega$, is obtained by multiplying Eq. (29) by the number of modes $Ad^2\vec{k}_\parallel^{(p)}/4\pi^2$ in the area $d^2\vec{k}_\parallel^{(p)}$. Since $\vec{k}_\parallel^{(p)} = \vec{k}_\parallel^{(0)} - \vec{k}_\parallel^{(s)} - \vec{G}_\parallel$, where $\vec{k}_\parallel^{(0)}$ is fixed, we have $d^2\vec{k}_\parallel^{(p)} = d^2\vec{k}_\parallel^{(s)}$. Thus, the current $\Delta J^{(s)}$ scattered into solid angle $\Delta\Omega$ with frequency shift in the range $\Delta\omega$ is

$$\Delta J^{(s)} = \delta J^{(s)} \frac{A}{4\pi^2} \frac{d^2\vec{k}_\parallel^{(s)}}{\Delta\Omega} \Delta\Omega\Delta\omega .$$

Following an earlier discussion,[10] it is a straightforward matter to show that the kinematical factor $d^2\vec{k}_\parallel^{(s)}/\Delta\Omega$ is given by

$$d^2\vec{k}_\parallel^{(s)}/\Delta\Omega = k^{(s)^2}\cos\theta_s \equiv mk^{(s)}v_z^{(s)}(\vec{g}_\parallel) ,$$

where θ_s is the angle made by the outgoing beam with the normal to the crystal surface. Thus, finally we have

$$\frac{\Delta J^{(s)}}{\Delta\Omega\Delta\omega} = \frac{mk^{(s)}v^{(s)}}{4\pi^2} \, |a_{\vec{k}_\parallel^{(s)}}(\vec{g}_\parallel)|^2 \times |M(\vec{k}_\parallel^{(0)}\mathcal{E}_0, \vec{k}_\parallel^{(s)}\mathcal{E}_s, \vec{k}_\parallel^{(p)}, \alpha)|^2 \rho(\vec{k}_\parallel^{(p)}, \omega_{\vec{k}_\parallel^{(p)},\alpha}) .$$

The cross section $d^2\sigma/d\Omega d\omega$ associated with the scattering process is obtained by dividing this result by the incident current. If, as mentioned earlier, $\psi^{(-)}_{\vec{k}_\parallel^{(0)}}$ is normalized so the single incoming component outside the crystal is $e^{i\vec{k}_0 \cdot \vec{r}}$, the incident current is just the group velocity $v^{(0)}$ of the incident beam in the present units. Since $v^{(0)}$ and $v^{(s)}$ are very nearly equal, we have

$$\frac{d^2\sigma}{d\Omega dw} = \frac{mk^s}{4\pi^2} \, |a_{\vec{k}_\parallel^{(s)}}(\vec{g}_\parallel)|^2 \, |M(\vec{k}_\parallel^{(0)}\mathcal{E}_0, \vec{k}_\parallel^{(s)}\mathcal{E}_s, \vec{k}_\parallel^{(p)}, \alpha)|^2 \times \rho(\vec{k}_\parallel^{(p)}, \omega_{\vec{k}_\parallel^{(p)},\alpha}) . \quad (30)$$

We next express the cross section in more convenient form. Let

$$\Gamma_{l_z l_z'}(\vec{k}_\parallel^{(s)}\mathcal{E}_s, \vec{k}_\parallel^{(0)}\mathcal{E}_0) = m_{l_z}(\vec{k}_\parallel^{(s)}\mathcal{E}_s, \vec{k}_\parallel^{(0)}\mathcal{E}_0)\, m^*_{l_z'}(\vec{k}_\parallel^{(s)}\mathcal{E}_s, \vec{k}_\parallel^{(0)}\mathcal{E}_0).$$

Then

$$\begin{aligned}\frac{d^2\sigma}{d\Omega d\omega} = \frac{N_s mk^{(s)}}{8\pi^2 M} \, |a_{\vec{k}_\parallel^{s}}(\vec{g}_\parallel)|^2 \sum_{l_z, l_z'} \Gamma_{l_z l_z'}(\vec{k}_\parallel^{(s)}\mathcal{E}_s, \vec{k}_\parallel^{(0)}\mathcal{E}_0) \\ \times [1 + n(\omega_{\vec{k}_\parallel^{(p)},\alpha})] \frac{1}{\omega_{\vec{k}_\parallel^{(p)},\alpha}} [\vec{Q}\cdot \vec{e}_{\vec{k}_\parallel^{(p)},\alpha}(l_z)] \\ \times [\vec{Q}\cdot \vec{e}_{\vec{k}_\parallel^{(p)},\alpha}(l_z')]^* \rho(\vec{k}_\parallel^{(p)}, \omega_{\vec{k}_\parallel^{(p)},\alpha}) . \quad (31)\end{aligned}$$

This result may be written in a more convenient form by introducing the phonon Green's function of the semi-infinite lattice. Following Maradudin and Wallis,[1] we let

$$U_{ij}(\vec{l}\,\vec{l}', \omega) = \frac{1}{M} \sum_s \frac{e_s^i(\vec{l})e_s^j(\vec{l}')}{\omega^2 - \omega_s^2} , \tag{31a}$$

where the index s refers to the quantum numbers of a mode of the semi-infinite crystal lattice and $e_s^i(\vec{l})$ is the ith Cartesian coordinate of the vector $\vec{e}_s(\vec{l})$. We write

$$U_{ij}(\vec{l}\,\vec{l}', \omega) = \frac{1}{N_s M} \sum_{\vec{k}_\parallel} U_{ij}(\vec{k}_\parallel, l_z l_z', \omega) e^{i\vec{k}_\parallel \cdot (\vec{l}_\parallel - \vec{l}_\parallel')} ,$$

where

$$U_{ij}(\vec{k}_\parallel, l_z l_z', \omega) = \sum_\alpha \frac{e^{i}_{\vec{k}_\parallel^{(p)*},\alpha}(l_z)\, e^{j}_{\vec{k}_\parallel^{(p)},\alpha}(l_z')}{\omega^2 - \omega^2_{\vec{k}_\parallel^{(p)},\alpha}} . \tag{31b}$$

Introduce the spectral density function

$$A_{ij}(\vec{k}_\parallel^{(p)}; l_z l_z'; \omega) = (1/i\pi)[U_{ij}(\vec{k}_\parallel, l_z l_z', \omega - i\eta) - U_{ij}(\vec{k}_\parallel, l_z l_z', \omega + i\eta)] .$$

The scattering cross section may be written conveniently in terms of the spectral density function:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{N_s m k^s}{8\pi^2 M} \left| a_{\vec{k}_\parallel^{(s)}}(\vec{g}_\parallel) \right|^2 [1 + n(\omega)] \times \sum_{l_z, l_z'} \Gamma_{l_z l_z'}(\vec{k}_\parallel^{(s)} \mathcal{E}_s, \vec{k}_\parallel^{(0)} \mathcal{E}_s) \times \sum_{ij} Q_i Q_j^* A_{ij}(\vec{k}_\parallel^{(p)}; l_z l_z'; \omega) , \tag{32}$$

where $\omega = \mathcal{E}_0 - \mathcal{E}_s$ is the energy lost by the electron.

The result displayed in Eq. (32) is the principal result of this section. In Sec. III, we shall employ a simplified form of this general result to explore the nature of the energy-loss spectrum and its sensitivity to the details of the lattice dynamics of the surface region of the crystal. The cross section for scattering by processes in which an electron gains energy by absorbing a phonon may be obtained from Eq. (32) by detailed balance considerations.

III. FORM OF ENERGY-LOSS SPECTRUM FOR MODEL CRYSTAL

In this section, we apply Eq. (32) to the analysis of the shape of the energy-loss spectrum, and its dependence of the lattice-dynamical properties of the surface region for a simple model crystal.

We shall first replace the general result exhibited in Eq. (32) by a simpler approximate form. As remarked above, a low-energy electron incident on the crystal samples only the region near the surface. As Duke and Tucker have pointed out,[9] this is so because electron-electron scattering produces a severe attenuation of the incident beam once it enters the crystal. We assume that to a first approximation, one may suppose that the incoming electron interacts only with the ions in the surface layer itself. Thus, in the sums over l_z and l_z' that appear in Eq. (32), we retain only the term with $l_z = l_z' = 0$. Thus,

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{N_s m k^s}{8\pi^2 M} \left| a_{\vec{k}_\parallel^{(s)}}(\vec{g}_\parallel) \right|^2 \Gamma_{00}(\vec{k}_\parallel^{(s)} \mathcal{E}_s, \vec{k}_\parallel^{(0)} \mathcal{E}_0) \times [1 + n(\omega)] \sum_{ij} Q_i Q_j^* A_{ij}(\vec{k}_\parallel^{(p)}; 0, 0, \omega) . \tag{33}$$

We will be interested primarily in the shape of the loss spectrum observed when the electrons are scattered into a particular outgoing direction by interacting with lattice vibrations of some particular wave vector $\vec{k}_\parallel^{(p)}$ parallel to the surface; i.e., for fixed $\vec{k}_\parallel^{(p)}$ we will study the dependence of the right-hand side of Eq. (33) on the energy loss ω. The factors on the first line are independent of ω, since $\mathcal{E}_s$ and $\mathcal{E}_0$ are nearly equal. Thus, for our purposes, we write

$$\frac{d^2\sigma}{d\Omega d\omega} = K[1 + n(\omega)] \sum_{ij} Q_i Q_j^* A_{ij}(\vec{k}_\parallel^{(p)}; 0, 0, \omega) , \tag{34}$$

where for fixed $\vec{k}_\parallel^{(p)}$, K is independent of energy transfer ω. To proceed, we need the value of the vector $\vec{Q}$. Recall from the discussion above that

$$\vec{Q}_\parallel = \vec{k}_\parallel^{(p)} , \tag{35}$$

while Q_z must be computed from Eq. (21) with $l_z = 0$. To compute Q_z, we thus need the value of the matrix element

$$\langle\langle \vec{k}_\parallel^{(s)}, \mathcal{E}_s | e^{iq_z z} e^{i\vec{G}_\parallel \cdot \vec{r}_\parallel} | \vec{k}_\parallel^{(0)}, \mathcal{E}_0 \rangle\rangle .$$

This matrix element will be calculated by employing a vastly oversimplified form for the wave function of the electron in the crystal. We presume that the effect of electron-electron interactions is to cause the effective wave function of the electron to assume a form in the crystal well approximated by a decaying exponential:

$$U_{\vec{k}_\parallel, \mathcal{E}}(\vec{r}_\parallel, z) = f_{\vec{k}_\parallel, \mathcal{E}}(\vec{r}_\parallel) e^{+\gamma z} \quad \text{for } z < 0 .$$

We also need the form of the Fourier transform $\tilde{v}(\vec{q})$ of the effective potential. As a matter of convenience, we take for this quantity the Fourier transform of a Yukawa potential:

$$\tilde{v}(\vec{q}) = \tilde{v}/(q_s^2 + q^2) ,$$

where the range of the potential in real space is $(q_s)^{-1}$. With this form for $\tilde{v}(\vec{q})$ and $U_{\vec{k}_\parallel, \mathcal{E}}(\vec{r}_\parallel, \mathcal{E})$, one readily obtains for Q_z the analytic form

$$Q_z = i(q_s^2 + \vec{k}_\parallel^{(p)2})^{1/2} . \tag{36}$$

To obtain the result of Eq. (36), one employs Eq. (21) for the case $l_z = 0$ and notes that

$$\vec{K}_\parallel = \vec{k}_\parallel^{(0)} - \vec{k}_\parallel^{(s)} + \vec{G}_\parallel = \vec{k}_\parallel^{(p)} .$$

The approximate expression for Q_z obtained by this procedure bears no resemblence to the expression that is produced by the kinematical theory. Notice that our expression for Q_z depends on the form of the scattering potential, since q_s enters Eq. (36)

explicitly.

Once the expression for Q_z is inserted into Eq. (34), the computation of the energy-loss spectrum reduces to the determination of the spectral density function $A_{ij}(\vec{k}_\parallel^{(p)}; 0, 0, \omega)$. We now turn to this question.

The spectral density function $A_{ij}(\vec{k}_\parallel^{(p)}; 0, 0, \omega)$ has been calculated for several values of $\vec{k}_\parallel^{(p)}$ and for a particular lattice-dynamical model. We have considered a fcc crystal with a free, unreconstructed (100) surface. The spectral density has been calculated by two methods. First we consider the case in which the atomic force constants in the surface layer assume a value identical to the bulk-crystal force constants. Then for a model with nearest-neighbor central-force interactions between the ions we have calculated the spectral density from the formal expression for the Green's function derived by Maradudin and Wallis,[1] and used by them to compute the surface specific heat of a simple cubic solid at low temperatures. We have also computed the spectral density directly from the eigenvectors associated with a slab of finite thickness (30 layers). In this instance, one can employ a computer to obtain accurate values of the phonon frequencies and the eigenvectors associated with a slab of infinite extent to two dimensions, and with a thickness of 30 layers normal to the surface.[11] With this second method, we have explored the effect of changes in the surface force constants and the range of the interaction on the shape of the loss spectrum, for various values of $\vec{k}_\parallel^{(p)}$. For a slab 30 layers thick, the surfaces are sufficiently far apart that one obtains a rather accurate approximation to the lattice-dynamical properties of the surface region of the semi-infinite medium.

We first describe the results of the work on the model of the semi-infinite crystal, using the Green's-function approach of Maradudin and Wallis. We shall consider a fcc crystal with a (100) surface, as mentioned above. The two-dimensional Brillouin zone appropriate to this crystal face is shown in Fig. 2. We have carried out calculations of the shape of the energy-loss spectrum for the ten values of $\vec{k}_\parallel^{(p)}$ indicated in the figure. For the case where the ions are coupled by nearest-neighbor central-force interactions, we give the bulk-phonon dispersion curves in Fig. 3. For each of the ten values of $\vec{k}_\parallel^{(p)}$ in the network of Fig. 2, we plot $\omega^2(\vec{k}_\parallel^{(p)}, k_z)$ for $0 < k_z < 2\pi/a_0$. The frequency units have been chosen so that the maximum frequency $\omega_{\max}$ of the crystal is 2. These curves will prove useful when we discuss the interpretation of the shapes assumed by the energy-loss spectrum.

Before presenting the results of the calculation, we make some comments on the numerical calculation. Maradudin and Wallis[1] write the Green's function $U_{ij}(\vec{l}\,\vec{l}', \omega)$ in the form

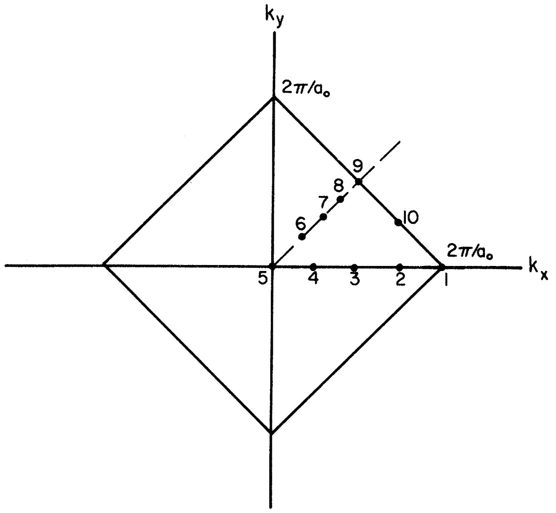

FIG. 2. Two-dimensional Brillouin zone appropriate to the fcc crystal, with a free (100) surface.

$$U_{ij}(\vec{l}\,\vec{l}', \omega) = \frac{1}{NM} \sum_{\vec{k}\lambda} \sum_{\vec{k}'\lambda'} e_i(\vec{k}\lambda)\, e_j^*(\vec{k}'\lambda')\, U(\vec{k}\lambda, \vec{k}'\lambda', \omega) \times e^{i\vec{k}\cdot\vec{l}'} e^{i\vec{k}'\cdot\vec{l}'}, \quad (37)$$

where $\vec{e}(\vec{k}\lambda)$ is the eigenvector of the infinitely extended crystal associated with the phonon of wave vector $\vec{k}$ and polarization λ. In Eq. (37), the notation differs slightly from that employed by Maradudin and Wallis. For the semi-infinite crystal, they demonstrate that

$$U(\vec{k}\lambda, \vec{k}'\lambda', \omega) = \delta_{k_x, -k_x'}\, \delta_{k_y, -k_y'} [\delta_{k_z, -k_z'}\, \delta_{\lambda\lambda'}\, U_0(\vec{k}\lambda, \omega) + U_0(\vec{k}\lambda, \omega)\, t(\vec{k}\lambda; \vec{k}'\lambda', \omega)\, U_0(\vec{k}'\lambda', \omega)], \quad (38)$$

where $t(\vec{k}\lambda, \vec{k}'\lambda', \omega)$ is the t matrix that describes the interaction of a phonon with the surface, and $U_0(\vec{k}\lambda, \omega) = [\omega^2 - \omega^2(\vec{k}\lambda)]^{-1}$. The function $U_{ij}(\vec{k}_\parallel^{(p)}, l_z l_z', \omega)$ may be expressed in terms of the result of Eq. (38):

$$U_{ij}(\vec{k}_\parallel^{(p)}, l_z l_z', \omega) = \frac{1}{L^2} \sum_{\substack{k_z k_z' \\ \lambda\lambda'}} e_i(\vec{k}_\parallel^{(p)} k_z, \lambda)\, e_j^*(\vec{k}_\parallel^{(p)} k_z', \lambda') \times U(\vec{k}_\parallel^{(p)} k_z, \lambda; \vec{k}_\parallel^{(p)} k_z', \lambda'; \omega) e^{ik_z l_z} e^{ik_z' l_z'}. \quad (38')$$

The length of a large cube within which periodic boundary conditions are imposed is L. By employing expressions derived by Maradudin and Wallis, the task of computing $U_{ij}(\vec{k}_\parallel^{(p)}, l_z l_z', \omega)$ can be reduced to that of evaluating certain functions of the form

$$G(\vec{k}_\parallel^{(p)}, \omega) = \sum_{k_z, j} \frac{f_j(\vec{k}_\parallel^{(p)}, k_z)}{(\omega + i\epsilon)^2 - \omega_j^2(\vec{k}_\parallel^{(p)} k_z)}, \quad (39)$$

where $\omega_j^2(\vec{k}_\parallel^{(p)} k_z)$ is the frequency of a phonon in the infinitely extended crystal with wave vector $\vec{k} = \vec{k}_\parallel^{(p)} + \hat{z} k_z$ and branch j. We refer the reader to the

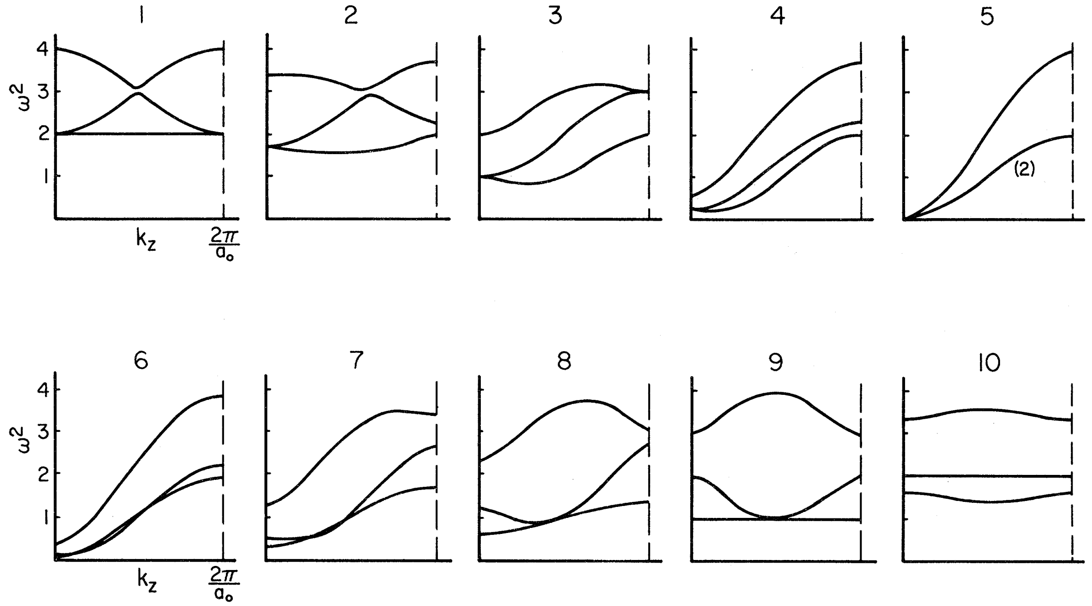

FIG. 3. For each of the ten points in the Brillouin zone of Fig. 2 we plot $\omega^2(\vec{k}_{\parallel}^{(p)}, k_z)$ for $0 < k_z < 2\pi/a_0$ for a fcc crystal with nearest-neighbor central-force interactions.

paper by Maradudin and Wallis[1] for the details. Since we encountered some difficulties evaluating the functions in Eq. (39) accurately, we shall make some comments about the procedures we employed.

In our first attempt, we chose a uniformly distributed set of values of k_z in the interval $-2\pi/a_0 < k_z < 2\pi/a_0$. The eigenvalues and eigenvectors were computed for each value of k_z. We then chose a small but finite value of ϵ (say, 5% of the maximum frequency of the crystal), and approximated the integral over k_z either by a Riemann sum or by the use of Simpson's rule. The notion was that if a sufficiently large number of k_z values were chosen, then the integral should be accurately approximated by this procedure and insensitive to the choice of ϵ, as it must be in the limit as $\epsilon \to 0$. This procedure appeared to work poorly, in the sense that the results did not appear insensitive to ϵ even when a large number (around 500) values of k_z were chosen. This is associated with the one-dimensional character of the integral. If the sum over k_z is replaced by an integral over frequency,

$$G(\vec{k}_{\parallel}^{(p)}, \omega) = \int d\omega' \, \rho(\vec{k}_{\parallel}^{(p)}, \omega') \frac{f}{(\omega + i\epsilon)^2 - \omega'^2}, \quad (40)$$

then the function $\rho(\vec{k}_{\parallel}^{(p)}, \omega')$ has square-root singularities characteristic of the density of phonons states for a one-dimensional lattice. Thus, even though one may choose a large number of k_z values when the integral in Eq. (39) is replaced by a sum, one obtains a much worse approximation to the integral than might be expected for the same size grid if the integral were smooth. This problem is presumably less severe for three-dimensional integrations in $\vec{k}$ space, where the density of modes is never singular.

We then turned to a different procedure. In the limit as $\epsilon \to 0$, one has for $\omega > 0$

$$\mathrm{Im}[G(\vec{k}_{\parallel}^{(p)}, \omega)] = -i \sum_j \sum_\alpha f_j(\vec{k}_{\parallel}^{(p)}, k_z) \Big/ \left(2 \left| \frac{\partial}{\partial k_z} \omega_j^2(\vec{k}_{\parallel}^{(p)} k_z) \right| \right) \Bigg|_{k_z = k_z^{(\alpha)}} . \quad (41)$$

The sum over α includes all values of k_z for which

$$\omega_j(\vec{k}_{\parallel}^{(p)}, k_z) = \omega .$$

The expression on the right-hand side of Eq. (4.1) may be accurately evaluated without encountering the above difficulties. This may be done by storing the phonon frequencies and eigenvectors associated with a grid of k_z values associated with a particular value of $\vec{k}_{\parallel}^{(p)}$, then approximating the derivative in Eq. (41) by a finite difference. This procedure turned out to be both simple and accurate.

We then obtain the real part of $G(\vec{k}_{\parallel}^{(p)}, \omega)$ by taking the Kramers-Kronig transform of the imaginary part. The same square-root singularities that appear in the density of modes $\rho(\vec{k}_{\parallel}^{(p)}, \omega)$ also appear in $\mathrm{Im}[G(\vec{k}_{\parallel}^{(p)}, \omega)]$, in many instances. To obtain accurate values of $\mathrm{Re}[G(\vec{k}_{\parallel}^{(p)}, \omega)]$ it was thus necessary to use a very fine grid in the vicinity of the singularities of $\mathrm{Im}[G(\vec{k}_{\parallel}^{(p)}, \omega)]$. In all the calculations reported below, care was taken to ensure that convergence had been obtained. There is also one point of the array in Fig. 2 (point 1) for which we can find an analytic form for the spectral density $A_{ij}(\vec{k}_\parallel^{(p)}, 0, 0, \omega)$. Thus, we could obtain a check on the accuracy of the numerical computation by comparing it with the analytic form obtained for point 1. The error in this numerical computation was found to be less than 1% except for frequencies very close to the singularity, where the real part of $U_{ij}(\vec{k}_\parallel^{(p)}, 0, 0, \omega)$ became somewhat less accurate.

We should also note briefly the value of q_s we used in obtaining Q_z from Eq. (36). We took q_s to be π/a_0, since we assumed the range of the interaction $1/q_s$ would be roughly equal to the radius of the ion, which is approximately a_0/π. The values $q_s = \pi/2a_0$, $\pi/4a_0$ associated with longer-range interactions were also used, and it was found that the qualitative shapes of the energy-loss spectra remained the same.

We shall now discuss the results of the analytic calculation done for point 1. At this point in the zone, $k_x = 2\pi/a_0$, $k_y = 0$, and the equations of motion of the infinite lattice are completely uncoupled so that the normal modes are all linearly polarized in the x, y, and z directions. As a consequence, there are no off-diagonal components of $U_{ij}(\vec{k}_\parallel^{(p)}, 0, 0, \omega + i\eta)$ for this point. All the z-polarized modes vibrate with frequency $\omega = \sqrt{2}$ using our scale, and they form the flat branch of the dispersion curves in Fig. 3. Each of these modes corresponds to a single layer of ions lying parallel to the surface vibrating while the other layers remain stationary. However, the ions in the surface layer interact only with the ones below them and hence vibrate at the lower frequency $\omega = 1$. This mode is the short-wavelength limiting form of the Rayleigh surface wave for this point in the zone. Since this is the only mode with a nonzero z component in the surface layer, we find

$$\mathrm{Im}[U_{zz}(\vec{Q}_\parallel^{(0)}, 0, 0, \omega + i\eta)] = \pi\delta(\omega^2 - 1) ,$$

where

$$\vec{Q}_\parallel^{(0)} = (2\pi/a_0, 0) .$$

We also find

$$\mathrm{Im}[U_{xx}(\vec{Q}_\parallel^{(0)}, 0, 0, \omega + i\eta)] = \mathrm{Im}[U_{yy}(\vec{Q}_\parallel^{(0)}, 0, 0, \omega + i\eta)]$$

$$= \left(\frac{4 - \omega^2}{\omega^2 - 2}\right)^{1/2} , \quad 2 < \omega^2 < 4$$

$$= 0 , \qquad \omega^2 < 2, \ \omega^2 > 4 .$$

In Fig. 4 we plot the energy-loss spectrum for point 1. It consists of a line corresponding to the surface mode and a part due to the bulk modes polarized in the x and y directions. The shape of the bulk contribution is due to two factors. We shall consider scattering produced by the x component of the surface ions' motion for $\vec{Q}_\parallel$ along the x direction. This means we need to consider $U_{xx}(\vec{Q}_\parallel, 0, 0, \omega + i\eta)$. This function is proportional to both the density of states $\rho(\vec{Q}_\parallel, \omega)$ of modes with a fixed wave vector $\vec{Q}_\parallel$ parallel to the surface and $|e_x(\vec{Q}_\parallel, \omega)|^2$, the square of the x component of the surface amplitude of the eigenvector corresponding to $\vec{Q}_\parallel$ and frequency ω. As we have mentioned above, there are square-root singularities in the density of states $\rho(\vec{Q}_\parallel, \omega)$. They occur at the bottom and top of the bulk bands, i.e., for $\omega_{\max}(\vec{Q}_\parallel)$ and $\omega_{\min}(\vec{Q}_\parallel)$, the maximum and minimum frequencies of the crystal for a given $\vec{Q}_\parallel$ directed along the x axis. In fact, we see in Fig. 4 that the energy-loss spectrum does exhibit the square-root singularity at $\omega_{\min}(\vec{Q}_\parallel)$ which arises from the singularity in $\rho(\vec{Q}_\parallel, \omega)$. However, we note that there is no such singularity at $\omega_{\max}(\vec{Q}_\parallel)$. Instead the cross section goes to zero. This is caused by the second factor, $|e_x(\vec{Q}_\parallel, \omega)|^2$. The eigenvector vanishes at the surface as $\omega \to \omega_{\max}(\vec{Q}_\parallel)$; at this frequency, a wave with displacement parallel to the surface reflects off with a 180° phase shift. This can be seen by examining the equations of motion for the lattice. The vanishing of the eigenvector suppresses the singularity that arises from the density of states. As $\omega \to \omega_{\min}(\vec{Q}_\parallel)$, the eigenvector remains finite; at this frequency, the wave is reflected with no change in phase. The singularity arising from the density of states will therefore be seen. As one can see from this example, the shape of the contribution to the spectrum from the bulk modes contains detailed information about the interaction of the bulk phonons

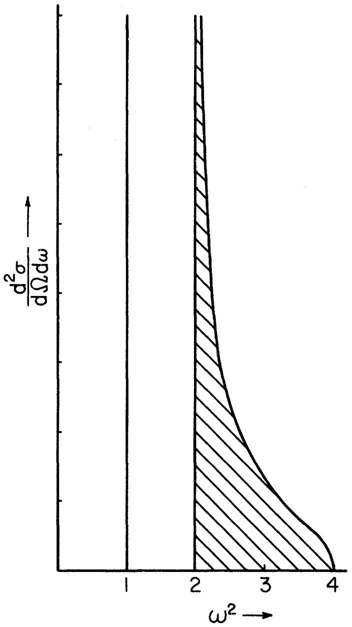

FIG. 4. Energy-loss spectrum appropriate to point 1 of Fig. 2, $\vec{k}_\parallel^{p} = (2\pi/a_0, 0)$.

with the surface. A study of both the bulk band and the position of the surface-mode peak thus gives one a complete picture of the nature of the vibration modes of the semi-infinite crystal with wave vector $\vec{Q}_{\parallel}$ parallel to the surface. We also note that the average bulk frequency seen by observing the bulk-mode scattering from the surface is lower than the mean bulk frequency of the crystal $\omega=\sqrt{3}$, as one can see from the asymmetry of the bulk contribution to the cross section. This is consistent with the fact that the mean-square amplitude of vibration of an atom in the surface is larger than the value appropriate to the bulk of the crystal.

Now we turn to the numerical studies of the energy-loss spectra for the values of $\vec{k}_{\parallel}^{(p)}$ indicated in Fig. 2. These spectra were calculated by evaluating the Green's function of Eq. (38′) on a computer using the method described earlier. The resulting loss spectra for six of the ten values of $\vec{k}_{\parallel}^{(p)}$ are displayed in Fig. 5. In the calculations, the crystal was assumed to be at room temperature, and $\omega_{\max}$ was chosen equal to the maximum vibration frequency of nickel. In general, there are contributions to the cross section from both the surface and bulk modes, as we have seen in Fig. 4. The positions of the loss peaks associated with the scattering by surface modes is indicated by the vertical arrows in Fig. 5. The relative strength of the scattering produced by the bulk and surface modes will be discussed below, when we examine the results for the finite slab.

The energy-loss spectra for points 9 and 10 at the edge of the Brillouin zone are particularly interesting, since for those values of $\vec{k}_{\parallel}^{(p)}$ there exists a gap between the two bulk bands, and a surface mode appears in the gap. Modes of this kind have been studied theoretically and discussed by deWette and co-workers.[12] Actually, at point 10 two other such surface modes exist, but they have a small amplitude at the surface. They make a very small contribution to the cross section as a consequence.

We shall now discuss the results we obtained by using the equations of motion of a 30-layer slab. Using a computer, it is straightforward to diagonalize the resulting 90×90 matrix and obtain all the normal-mode frequencies and eigenvectors. One can then compute the spectral density directly from Eq. (31b). This method is a particularly convenient one for studying the effects of changing force constants near the surface because it is quite simple to adjust them in the program. It is also helpful in studying surface modes because one can examine the eigenvectors explicitly with little effort. This method does have a major drawback. The spectral density found in this way is a series of δ-function peaks which then must be added together to form histograms if the information is to be presented in simple form. Although it is impossible to obtain extremely detailed information about the shape of the bulk-mode contribution to the cross sections from the histograms, one can easily identify the same general features of the spectra that were obtained by our first method and displayed in Fig. 5. The surface-mode frequencies and their strengths are also easily found. Upon changing the force constants in the surface, one can then easily visualize the qualitative changes in the spectra of Fig. 5 by following the changes in the histograms.

The first change we made in the simple model of the fcc crystal with a (100) surface and nearest-neighbor central-force interactions was to add next-nearest-neighbor central-force interactions. Again we used values of the force constants so that the elastic constants approximate those of Ni. The ratio B of the next-nearest-neighbor force constant to the nearest-neighbor force constant was found to

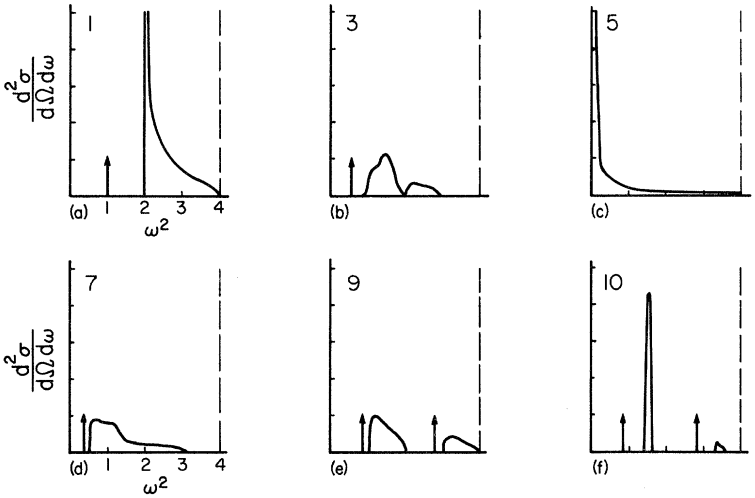

FIG. 5. Energy-loss spectra for six of the ten values of $\vec{k}_{\parallel}^{p}$ displayed in Fig. 2. These spectra were calculated by numerical evaluation of the Green's function for the semi-infinite crystal and for geometry described in the text.

be −0.0308. In the work that follows, B will always have this value (rather than zero as before) unless it is specifically changed. This addition of next-nearest-neighbor interactions changed the loss spectra very little.

The second change we made was to change the nearest-neighbor force constant between the first and second layers so that the surface layer was bound more or less tightly to the rest of the crystal. We define C to be the ratio of the force constant between layers 1 and 2 to the bulk nearest-neighbor force constant, and we employed the values $C = 0.5$, 0.75, 1.0 and 1.25.

In Fig. 6 we display loss spectra for two of the values of $\vec{k}_{\parallel}^{(p)}$ to demonstrate the changes occurring in the cross sections when the strength of the interaction between the first and second layers is varied. One can see a general shift of the bulk scattering strength to the lower-frequency ends of the respective bands as this surface force constant is decreased. The surface-mode contributions are also shifted to lower frequencies and increased in strength relative to the bulk-mode scattering. This is particularly evident for point 9, where the ratio of surface scattering to bulk scattering significantly increases when the surface layer becomes less tightly bound. However, the effect of changing the surface force constant is more easily measurable by looking at scattering with $\vec{k}_{\parallel}^{(p)} = (2\pi/a_0,\ 0)$ (point 1). As mentioned above, the surface mode for this value of $\vec{k}_{\parallel}^{(p)}$ consists only of the surface layer vibrating normal to the surface, and all other layers remain stationary. Hence, when the force constant between the first and second layers is changed, the frequency of the surface mode shifts accordingly. In fact, using our frequency scale, $\omega^2 = C$ as can be seen in Fig. 6. (Actually ω^2 is not quite equal to C because of the next-nearest-neighbor interactions that have been added to our model, but the shift is very small and the surface-mode frequency provides an accurate estimate of C.)

As the third change in our model of the semi-infinite slab, we let the nearest-neighbor force constants *within* the surface layer become different from those of the bulk crystal. This change affected only force constants between atoms lying parallel to the surface and was quite different in its effect from the previous change of force constants

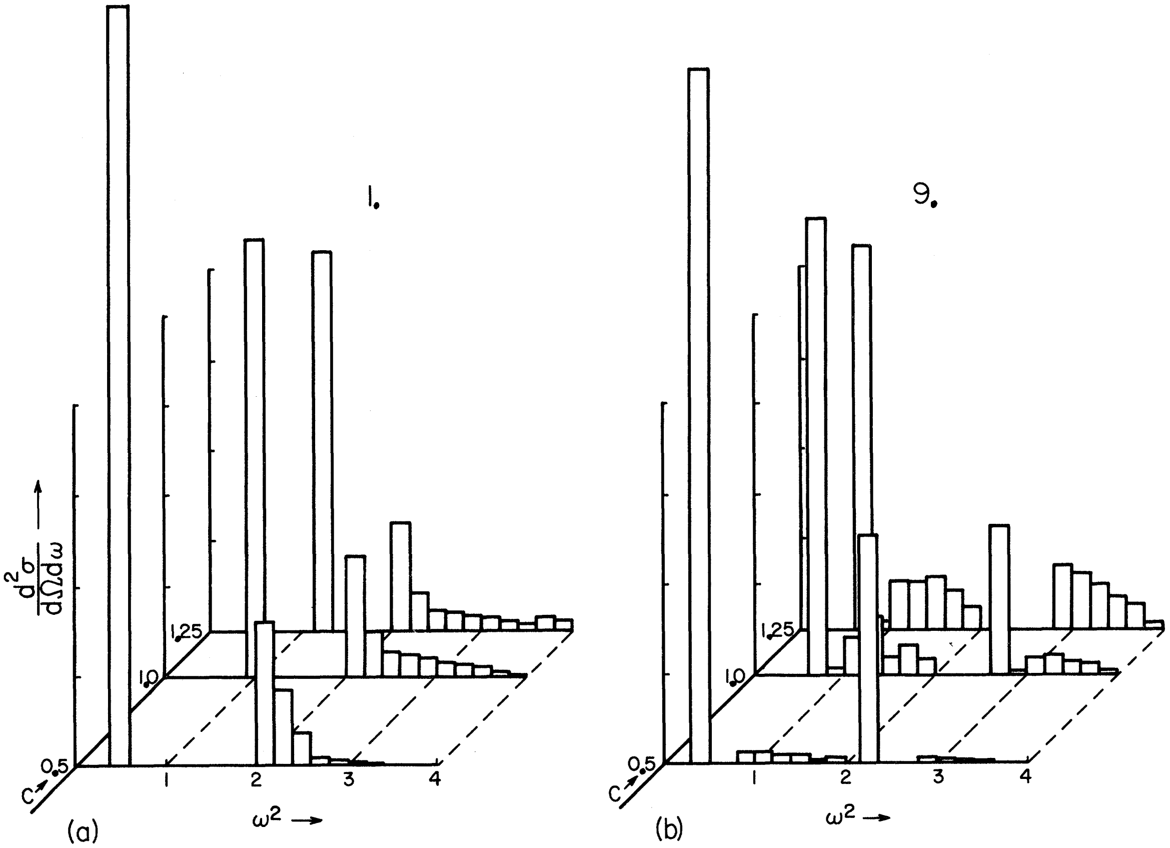

FIG. 6. Energy-loss spectra for (a) point 1 and (b) point 9 of Fig. 2. The spectra are calculated for three values of the ratio C of the atomic force constants between the first and second layers of the crystal to the bulk value of this quantity. The spectra were calculated from the study of scattering from a 30-layer slab of material.

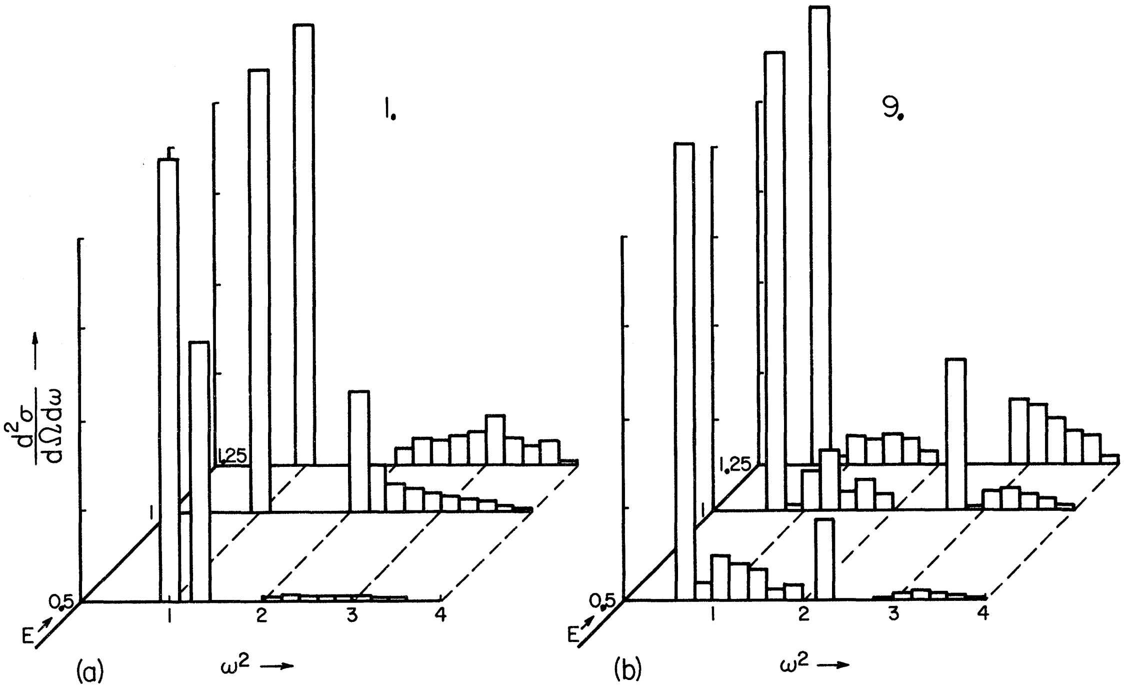

FIG. 7. Energy-loss spectra for (a) point 1 and (b) point 9 of Fig. 2, for three different values of the ratio E of the nearest-neighbor force constants within the surface layer to the value appropriate to the bulk.

between the first and second layers. We define the quantity E to be the ratio of the nearest-neighbor force constant within the surface layer to the nearest-neighbor force constant for the bulk crystal, and we let E range from 0.5 to 1.25.

In Fig. 7 we display the energy-loss spectra appropriate to points 1 and 9 in the Brillouin zone. These were obtained by letting E take on the values 0.5, 1.0, and 1.25. The primary trend as the force constants within the surface layer are decreased is that the higher-frequency bulk contributions to the cross sections become much smaller. For both values of $\vec{k}_{\parallel}^{(p)}$ used here, the lowest-frequency surface mode contributing to the loss spectra is z polarized. These modes remain unchanged because changing E changes only the forces in the x and y directions. However, the other (x- and y-polarized) surface modes are strongly affected. In fact, one can see that for point 1 a new surface mode is created as E is lowered. The shape of the bulk band contribution is also significantly changed. As E is changed from its original value of unity, the surface amplitudes of the eigenvectors for frequencies near the bottom of the bulk band for point 1 tend toward zero. Hence the singularities arising from the density of states (as discussed above) are suppressed as one approaches both the minimum and maximum frequencies of the bulk crystal. Again we see that one may obtain information about the eigenvectors from the shape of the bulk loss spectra. Finally, we note that both the shape of the bulk contribution and the position of the second surface mode give us information concerning the quantity E.

We should mention here that we also tried adding larger next-nearest-neighbor interactions in order to see what qualitative changes would occur. As B, the ratio of the next-nearest-neighbor to the nearest-neighbor force constants, was made more negative, the crystal became unstable. Therefore we used the values $B = -0.10$, where the crystal was found to be stable, and $B = +0.25$. There were no large qualitative changes in the energy-loss spectra.

TABLE I. Ratio of the integrated intensity of the surface-mode peak to the total differential cross section per unit solid angle, for various force-constant configurations.

Point in zone	$B = -0.0308$ $C = E = 1$	$C = 0.50$	$C = 1.25$	$E = 0.50$	$E = 1.25$	$B = 0.25$	$B = -0.10$
1	0.63	0.73	0.59	0.96	0.64	0.61	0.64
9	0.71	0.92	0.46	0.72	0.56	0.85	0.65

Basically, as B increased (positively), there was a shift of the spectra upward in frequency. For some values of $\vec{k}_{\|}^{(p)}$ there was also an increase in the amount of scattering from the surface modes relative to the bulk scattering.

We would now like to comment on the strength of the scattering from the surface modes. It is difficult to obtain a realistic estimate of the percentage of the total scattering that is due to scattering from the surface modes, since the value of Q_z employed in the present work is very approximate. In Table I we indicate this percentage for points 1 and 9 in the zone and for the various force-constant configurations described earlier. One can see that in most cases the surface modes and the integrated strength of the bulk-mode contribution contribute almost equally to the total cross section. Of course, at point 5, the origin of the Brillouin zone, there are no surface modes and hence all the scattering is from bulk modes. Except for values of $\vec{k}_{\|}^{(p)}$ close to the origin, the surface scattering is comparable in strength to the total bulk scattering for most cases examined; as the force constants near the surface are softened, note that the intensity of the surface-mode scattering increases relative to the bulk in a pronounced manner.

We conclude this section by stressing that the study of inelastic electron scattering from crystal surfaces has the potential of mapping out in great detail the frequency spectrum associated with the vibration of surface atoms. As we have seen, the shape of the loss spectrum is very sensitive to changes in the atomic force constants near the surface. As we see in Figs. 6 and 7, the shape of the spectrum depends qualitatively on the precise manner in which the surface force constants and bulk force constants differ. While we have examined the case in which certain force constants are stiffened or softened, the work of Wallis and co-workers[13] suggests that one may expect the atomic-force constants to be weaker in the surface, compared to the values appropriate to the bulk.

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