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Theory of Inelastic Processes in Low-Energy Electron-Loss Spectroscopy. II. The Optical Potential

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The optical potential for an electron interacting with a semiinfinite dielectric is evaluated. The potential includes both bulk- and surface-plasmon contributions. It is found that the potential makes a substantial contribution to the reflectivity of the surface.

INTRODUCTION

Experimental studies of the interaction of electron beams with solids could provide valuable information about the nature of the surface of the solid. This is particularly true at low energies, where the penetration of the electron beam does not extend beyond the first few atomic layers. This penetration is inhibited by two effects: the so-called primary extinction of the incident beam and the inelastic excitation processes. In the former case, unitarity of the scattering matrix demands that as electrons are Bragg scattered out of the incident wave its amplitude must decrease. Since electrons are strongly deflected at low energies, this is an effective damping mechanism. The inelastic processes also severely limit the penetration as the electrons tend to excite bulk plasmons, surface plasmons, and phonons.

In a previous paper[1] (hereafter referred to as I) a formalism was introduced which enabled the treatment of inelastic processes in low-energy electron-loss spectroscopy by Feynman-diagram techniques. In particular, it was found that there exists an optical potential which is describable in terms of the dielectric properties of the solid. The concept of optical potentials in low-energy electron-diffraction (LEED) problems has been employed before.[2] In previous computations, however, only a bulk optical potential was utilized.[3] As demonstrated in I, the optical potential for a semiinfinite dielectric assumes a somewhat different form from that for a homogeneous dielectric. We therefore thought it worthwhile to present the computation for the optical potential for a bounded dielectric. This could then be used as an input to more sophisticated LEED or inelastic-loss-spectroscopy calculations.[4]

In Quinn's derivation of the optical potential,[3] a fully quantum-mechanical approach was employed. The self-energy of an electron moving in a dielectric medium was evaluated and an appropriate optical potential was extracted. In I, we have shown how this optical potential could be obtained directly from Maxwell's equations if semiclassical arguments are employed.[5] The optical potentials for the infinite dielectric agreed exactly. For the semiinfinite dielectric, we found a somewhat different expression which could be interpreted as the bulk potential plus a surface optical potential. The surface optical potential was taken to be localized at the surface. Physically we expect the latter potential to be confined to within a few atomic spacings of the surface.[6] As the dielectric function has no real meaning for distances smaller than this, we simply treated it as a δ function at the surface.

The evaluation of the potential in this paper closely parallels the calculation of the bulk optical potential made by Quinn.[3] The dielectric properties of the solid are taken to be those of a "Jellium" model with the same Fermi energy. Thus, it is the Lindhard dielectric constant which enters our formulas. All anisotropic effects are neglected except for the presence of a boundary. While other dielectric functions may be employed, they would undoubtedly entail additional computational effort. Therefore, as a first attempt at a crude understanding of the solid, we try this simplest case.

THEORY

Imagine the crystal to be oriented so that the outward normal is directed along the $\hat{Z}$ axis. The expression derived in I for the optical potential of a semiinfinite dielectric is

$$U_{\rm opt} = \alpha(E)U(Z) + \beta(E,\psi)\delta(Z), \quad (1)$$

where

$$\alpha(E) = (e^2/2\pi^2)\int d\omega \int d^3q\,(1/q^2) \times \delta(\omega - \vec{q}\cdot\vec{v})\,(1/\epsilon - 1), \quad (2)$$

$$\beta(E,\psi) = (e^2/2\pi^2)\int d\omega \int d^3q (q_\perp/q^4) \times \delta(\omega - \vec{q}\cdot\vec{v})[4/(1+\epsilon) - 1 - 1/\epsilon]. \quad (3)$$

$U(Z)$ is a function which assumes the value unity within the solid and vanishes outside the solid. Both α and β depend on the incident particle's energy. Furthermore, β depends on the angle which the incident particle makes with the surface. In the above equations, ϵ is the (complex) Lindhard dielectric function, $q_\perp$ is the component of $\vec{q}$ along the solid's surface, and $\vec{v}$ is the velocity of the electron.

We shall be primarily interested in the imaginary part of the optical potential since it represents the effect of inelastic processes (plasmon production and electron-hole excitation). The real part of the potential is a somewhat more difficult quantity to get a handle on because it invariably involves the work function and the detailed description of the structure of the surface. In fact, if one formally tried to evaluate Reα and Reβ one would run into difficulty. While Reα yields a finite result, Reβ diverges logarithmically. This would seem to imply the need for a low-momentum cutoff – perhaps near the shielding radius. The imaginary parts of α and β, on the other hand, are well-defined. This is reminiscent of the calculation of the level shift (Lamb shift) and width (lifetime) of atomic energy levels. For methods used in the literature to describe the real potential we refer to Ref. 4.

It is convenient to work in units where $\hbar = 1, e^2 = 2$, and $2m = 1$. Then energy is measured in Rydberg units and distances in Bohr radii.

The surface optical potential β may be regarded as being composed of contributions from elementary processes in which an electron of momentum $\vec{p}$ enters, transfers momentum $\vec{q}$ to the solid, and propagates with momentum $\vec{p}\,' = \vec{p} - \vec{q}$. The δ function in Eq. (3) then informs us that energy is conserved, provided we interpret the velocity as

$$\vec{v} = (1/2m)(\vec{p} + \vec{p}\,') = \vec{p} + \vec{p}\,'. \quad (4)$$

Indeed this result would also be obtained if we treated $\vec{v}$ as the conventional current operator acting between plane-wave states. Thus we obtain

$$\beta = (1/\pi^2)\int d\omega \int d\phi \int d\theta \sin\theta \int dq\; q_\perp/q^2 \times \delta(\omega - 2\vec{p}\cdot\vec{q} + \vec{q}^{\,2})[4/(1+\epsilon) - 1 - 1/\epsilon]. \quad (5)$$

The geometry of the problem is illustrated in Fig. 1. Note that

$$q_\perp = (q^2 - q_Z^2)^{1/2}, \quad (6a)$$

$$q_Z = q(\sin\theta \sin\psi \cos\phi + \cos\theta\cos\psi). \quad (6b)$$

For convenience of notation, the azimuthal integral is denoted by

$$I(\theta,\psi) = \int_0^{2\pi}(q_\perp/q)\,d\phi = \int_0^{\pi}[1 - (\sin\theta\sin\psi\cos\phi + \cos\theta\cos\psi)^2]^{1/2}\,d\phi. \quad (7)$$

For normal incidence, $\psi = 0$, and we have simply $I = 2\pi\sin\theta$. In other cases, I can be expressed in terms of elliptic functions. We also have the symmetry property $I(\theta,\psi) = I(\theta, \pi - \psi)$. This tells us that the optical potential is time-reversal invariant. Upon performing the frequency integration, we obtain

$$\mathrm{Im}\beta = \left(\frac{1}{\pi}\right)^2 \int dx \int \frac{dq}{q}\, I(\theta,\psi)\, \mathrm{Im}\left(\frac{4}{1+\epsilon} - \frac{1}{\epsilon}\right), \quad (8)$$

where $x = \cos\theta$ and the integrand is to be evaluated at

$$\omega = 2pqx - q^2 + i\delta. \quad (9)$$

The imaginary infinitesimal part tacked onto ω provides us with a prescription for going around the poles.[3]

It is convenient to introduce the substitutions

$$Z = q/2q_0, \quad (10a)$$

$$W = p/q_0, \quad (10b)$$

$$U = Wx - Z, \quad (10c)$$

where q_0 is the Fermi momentum, the corresponding Fermi energy being q_0^2. We must now specify the domain of integration of the variables x and Z.

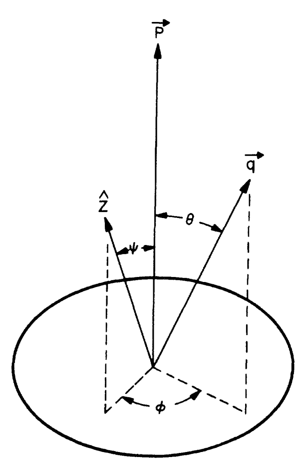

FIG. 1. Geometry for problem.

Clearly the energy loss ω must be bracketed between zero and the height of the initial energy above the Fermi sea, $E-E_0$. This prevents the electron from collapsing into the Fermi sea and consequently violating the Pauli exclusion principle. Thus, in terms of the reduced variables, we have

$$Z/W \le x \le Z/W + (W^2-1)/4ZW. \tag{11a}$$

In addition, the bounds on the cosine function require

$$|x| \le 1. \tag{11b}$$

The domain of integration is sketched in Fig. 2. The roots Z_1 and Z_2 defined there are given by

$$Z_1 = \tfrac{1}{2}(W-1), \tag{12a}$$

$$Z_2 = \tfrac{1}{2}(W+1). \tag{12b}$$

The Lindhard dielectric function is given by

$$\epsilon = \epsilon_1 + i\epsilon_2, \tag{13}$$

where

$$\epsilon_1 = 1 + (8\pi q_0 Z^3)^{-1}\{4Z + [1-(Z-U)^2] \times \ln|(U-Z-1)/(U-Z+1)| + [1-(Z+U)^2]\ln|(U+Z+1)/(U+Z-1)|\}, \tag{14a}$$

$$\epsilon_2 = (8Z^3 q_0)^{-1} \times \begin{cases} 0 & \text{if } U > Z+1 \\ 1-(Z-U)^2 & \text{if } |Z-1| < U < Z+1 \\ 0 & \text{if } U < Z-1 \text{ and } Z>1 \\ 4ZU & \text{if } U < 1-Z \text{ and } 0<Z<1. \end{cases} \tag{14b}$$

In Fig. 2 we have denoted by a dashed line the equation $U = Z+1$. Above this line the imaginary part of the dielectric constant vanishes. In this region there may exist lines on which ϵ_1 or $\epsilon_1 + 1$ vanish.

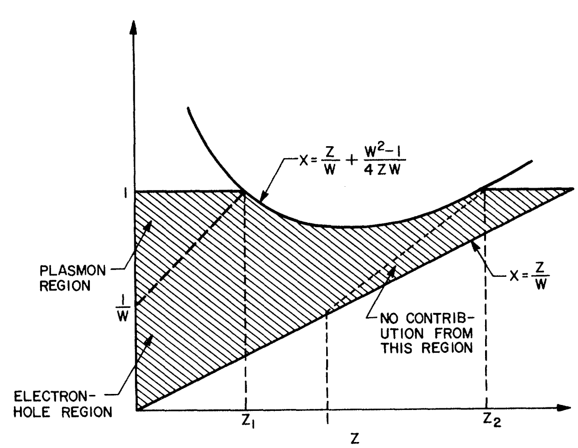

FIG. 2. Domain of integration.

These correspond to the bulk and surface plasmons, respectively. As seen from Eq. (8) these result in poles in the integrand. One only obtains contributions from these poles above the plasmon thresholds.

We first consider the contribution to the surface optical potential stemming from surface plasmons. Let $Z = B(x)$ be the solution to the equation

$$\epsilon(B,x) + 1 = 0. \tag{15}$$

In the neighborhood of $Z = B(x)$, we can expand the dielectric function

$$\epsilon(Z,x) + 1 = [Z - B(x) + i\delta]\frac{\partial\epsilon_1}{\partial Z}\bigg|_{Z=B} + O(Z-B)^2. \tag{16}$$

The sign of the imaginary term $i\delta$ is chosen so that the potential will be absorptive. Thus the surface-plasmon contribution is

$$\mathrm{Im}\beta_1 = -\frac{4}{\pi}\int_{x_B}^{1} dx\, I(\theta,\psi)/B(x)\frac{\partial\epsilon_1}{\partial Z}\bigg|_{Z=B}. \tag{17}$$

x_B is that point where the surface-plasmon line intersects the dashed line of Fig. 2. Thus x_B is the simultaneous root of Eq. (15) and

$$Wx = 2B+1. \tag{18}$$

From Eq. (14a) we can extract an analytic expression for the denominator of the integrand of Eq. (17). Thus, we have

$$Z\frac{\partial\epsilon_1}{\partial Z} = -3(\epsilon-1) + (8\pi q_0 Z^2)^{-1} \times \left[8 + 4(U-Z)\ln\left(\frac{U-Z-1}{U-Z+1}\right)\right]. \tag{19}$$

Similarly we may compute the contribution stemming from the bulk plasmon. Letting $Z = A(x)$ be the solution to

$$\epsilon(A,x) = 0 \tag{20}$$

and proceeding as before, we obtain

$$\mathrm{Im}\,\beta_2 = \frac{1}{\pi}\int_{x_A}^{1} dx\, I(\theta,\psi)/A(z)\frac{\partial\epsilon_1}{\partial Z}\bigg|_{Z=A}. \tag{21}$$

Physically, this represents a correction to the bulk optical potential due to the presence of a surface. The quantity x_A is the simultaneous solution of Eqs. (18) and (20).

Our final contribution to the optical potential arises from electron-hole-pair excitations. To find this component a double integration must be performed:

$$\mathrm{Im}\,\beta_3 = -\frac{1}{\pi^2}\iint dx\,dz\,\frac{I(\theta,\psi)}{Z}\left[\frac{4\epsilon_2}{(1+\epsilon_1)^2+\epsilon_2^2} - \frac{\epsilon_2}{\epsilon_1^2+\epsilon_2^2}\right], \tag{22}$$

The domain of integration is given by

$$\max\left[\frac{2Z-1}{W}, \frac{Z}{W}\right] \le x \le \min\left[1, \frac{Z}{W} + \frac{W^2-1}{4ZW}\right], \qquad (23)$$

$$0 \le Z \quad \tfrac{1}{2}(W+1). \qquad (24)$$

Equations (17), (21), and (22) are combined to give the total surface optical potential.

The threshold condition corresponds to the case where x_A or x_B rises to unity. Thus the threshold momentum W is the root of the equation

$$\pi q_0(1+c) = (W-1)^{-2}\{-2+(W+1)\ln[(W+1)/(W-1)]\} \qquad (25)$$

where $C=1$ for surface plasmons, and $C=0$ for bulk plasmons.

The thresholds are plotted as a function of the Fermi energy in Fig. 3. A typical pair of plasmon dispersion curves is illustrated in Fig. 4. As mentioned earlier, the plasmon exists in the region where the dielectric constant is real. Although, as shown in Fig. 2, there are two domains where the imaginary part vanishes, one of these domains has no zeros for the dielectric function. The plasmon dispersion curves end abruptly at the dashed line in Fig. 4, which represents the boundary of the electron-hole-excitation region. Undoubtedly, in a more sophisticated treatment of the solid surface, the bulk and plasmon curves could look somewhat different. However, our goal here is to explore the simplest model with the intention of seeing how far one can carry it and just where it falters.

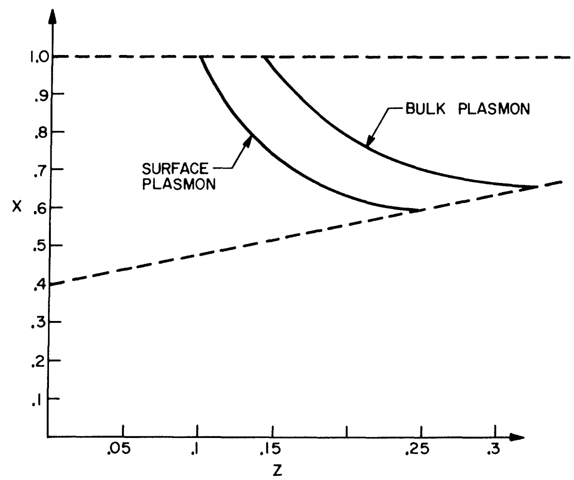

FIG. 4. Plasmon dispersion curves: $q_0=0.96$, $W=2.50$.

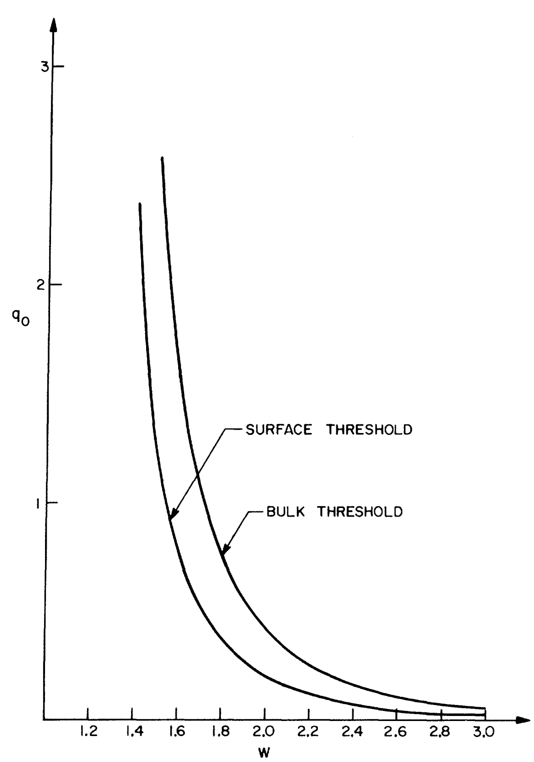

FIG. 3. Plasmon thresholds.

RESULTS AND DISCUSSION

In the previous section the explicit expressions for the optical potential of Eqs. (1)–(3) were recast into a form in which it is convenient to perform calculations. The actual computations were made on a digital computer and the results are presented in Figs. 5–7. In Fig. 5 the surface optical potential is displayed for a Fermi energy of 1 Ry and for the case where the electron impinges on the solid at normal incidence. Following Quinn,[3] we show the plasmon-pole contribution and the electron-hole contribution separately, as well as their sum. Note that there are two thresholds for plasmon production, one corresponding to the bulk plasmons, at approximately $W=1.72$, and the other corresponding to surface plasmons, at approximately $W=1.56$. These thresholds do not occur at exactly the plasmon frequencies because conservation of momentum introduces a laboratory frame to center-of-mass frame conversion. The electron-hole contribution is seen to peak at roughly 1.8 a.u. and then slowly decay at higher energies. On the other hand, the plasmon contribution seems to be monotonically increasing, at least for moderately low energies. Thus, at high energies it is the plasmon which dominates the surface optical potential.

In Fig. 6 we have plotted, for comparison, the bulk optical potential. Of course this is independent of the angle of incidence. While the curves appear quite similar, the bulk optical potential has a peak at roughly 2.5 a.u. and then decays slowly at higher energies. It should also be pointed out that the units of the two curves are different, so a rigorous comparison should not be attempted.

Finally, Fig. 7 displays the dependence of the surface optical potential on the angle of incidence.

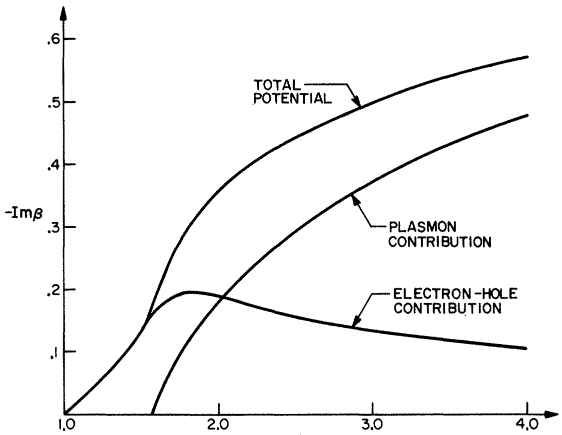

FIG. 5. Surface optical potential: $q_0=1$, $\Psi=0$.

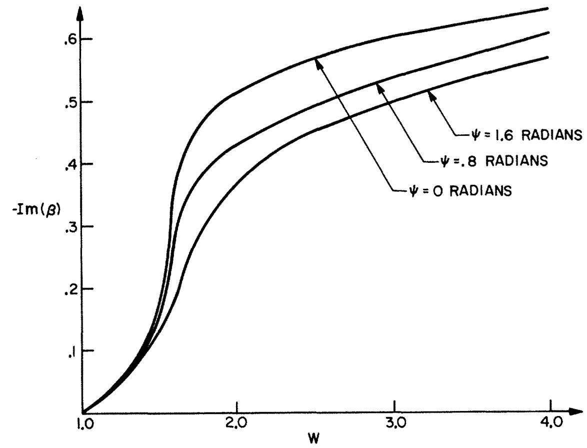

FIG. 7. Surface optical potential for several Ψ values.

We note that there is as much as a 20% variation in the potential as ψ ranges between 0 and $\frac{1}{2}\pi$ rad. As the angle of incidence made with the normal is increased, the potential also increases. This effect may be qualitatively understood by realizing that the electron spends more time in the vicinity of the surface in such a case. Thus it has more opportunity to excite surface plasmons. Indeed the largest variation appears for those energies above threshold, whereas below threshold the potentials are practically identical.

To obtain some feeling for the importance of the surface optical potential, we consider an idealized model. Consider a semiinfinite dielectric block upon which electrons impinge. All real potentials in the block will be neglected and it will be assumed to be endowed only with a bulk and surface (imaginary) optical potential. The reflection coefficient will be calculated for two cases: one with both the surface and bulk potentials present and one with only the bulk potential present. For simplicity we will only do this for normal incidence, although the model can be generalized quite readily.

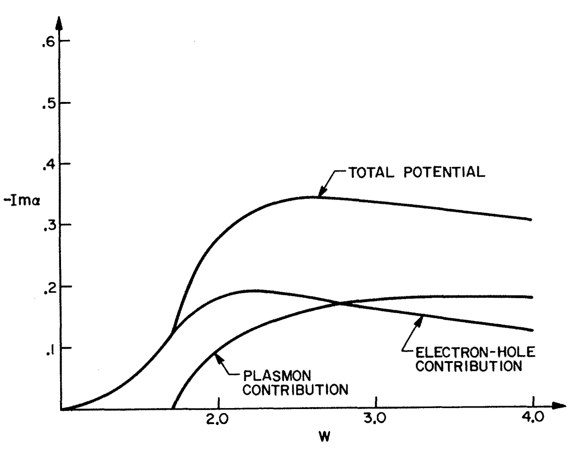

FIG. 6. Bulk optical potential: $q_0=1$.

The Schrödinger equation for the problem is

$$[-d^2/dZ^2 - i\tilde{\alpha}(E)U(Z) - i\tilde{\beta}(E,\psi)\,\delta(Z) - E\,]\,\psi(Z)=0\ , \tag{26}$$

where we have let $\alpha=-i\tilde{\alpha}$ and $\beta=-i\tilde{\beta}$. The quantities $\tilde{\alpha}$ and $\tilde{\beta}$ are, therefore, positive numbers. The solution to this one-dimensional problem is simply

$$\psi(Z)=\begin{cases} Ae^{\gamma Z}, & Z<0 \\ e^{-ipZ}+Re^{ipZ}, & Z>0, \end{cases} \tag{27}$$

where the solid is taken to fill the half-space $Z<0$. Continuity of the wave function at the boundary implies

$$A=1+R, \tag{28}$$

while the discontinuity in the slope requires that

$$A(\gamma - i\tilde{\beta})=ip(R-1). \tag{29}$$

Inserting Eq. (27) into (26) gives us an explicit expression for γ:

$$\gamma=-i(p^2+i\tilde{\alpha})^{1/2}\ . \tag{30}$$

The negative root is taken because this gives no reflection when the potentials vanish. Thus the reflection amplitude is

$$R=[p-(p^2+i\tilde{\alpha})^{1/2}-\tilde{\beta}]/[p+(p^2+i\tilde{\alpha})^{1/2}+\tilde{\beta}]\ . \tag{31}$$

The physically measurable reflection coefficient is given by the absolute square of the amplitude

$$r=|\,R\,|^2. \tag{32}$$

The results are plotted in Fig. 8 for two cases. In one case both $\tilde{\alpha}$ and $\tilde{\beta}$ are nonvanishing, whereas in the other case $\tilde{\beta}$ is set equal to zero. The $\tilde{\alpha}$ and $\tilde{\beta}$ functions are plotted in Figs. 5 and 6 and

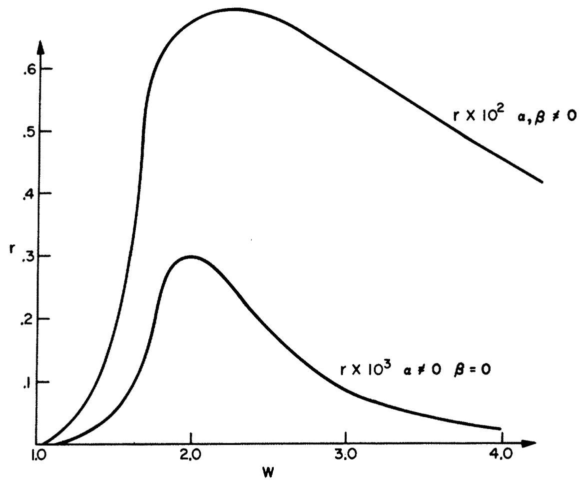

FIG. 8. Reflection coefficient for two cases.

correspond to a Fermi momentum of $q_0 = 1$. This would be roughly appropriate for a metal like aluminum. We do not expect a very sensitive dependence of our results on the Fermi momentum. For this reason we believe that the conclusions reached in this paper should be applicable to a broad class of metals. We notice a rather startling alteration of the reflection coefficient due to the presence of the surface. The reflectance is increased by more than an order of magnitude when the absorptive surface potential is included. That this is plausible might be seen as follows. Consider the reflection amplitude of Eq. (31) in the case where $\tilde{\beta} = 0$. Then, since $\tilde{\alpha} \ll p^2$, we have

$$R = [p - (p^2 + i\tilde{\alpha})^{1/2}]/[p + (p^2 + i\tilde{\alpha})^{1/2}] \approx -i\tilde{\alpha}/4p^2. \quad (33)$$

One might think of the inclusion of a surface as equivalent, in some sense, to increasing the absorptivity of the medium. From Eq. (33) we see that as a is increased, so is R. Furthermore, since the surface potential is localized at the surface, it interacts with the full incident wave and so exerts a large influence on it. Thus it is reasonable that when β is included R should increase considerably. One might also draw an analogy between reflection from an absorptive surface and scattering from an absorptive sphere.[7] In the case of the sphere it is known that a black sphere presents an equal cross section for absorption and elastic scattering, whereas a gray sphere has diminished elastic scattering. The analog of elastic scattering for our problem is reflectance. Thus the results are consistent.

We notice that an appreciable reflectance on the order of 0.7% occurs when the effect of surface plasmons is included. Of course, before one can obtain a theory to compare with experiment, the all-important Bragg scattering effects must be included. It is interesting, however, to compare the "bare" reflectance of our dielectric block with the reflectance of a typical metal. Khan, Hobson, and Armstrong[8] have measured the reflectance of various tungsten faces as a function of electron energies. For the 100 face it is found that the reflectance drops from around 10% at 20 V to 2% at 40 V. Thus at higher energies the effects of surface-plasmon stimulation become increasingly important and must be included in realistic calculations. In addition we expect the optical potential to have a large effect on the width of LEED diffraction peaks. Thus we conclude that the reflectances in solids depend rather strongly on the surface optical potential.

We hope, in the near future, to perform a LEED calculation with Bragg scattering and the full optical potential included. This could then be confronted against existing experiments.

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