that the above ratio will drop continuously to zero when $\kappa \to 1/\sqrt{2}$, whereas the experimental ratio levels off at a constant value similar to our ratio $R(H_c^+)/R_n$. The theoretical model due to Rothwarf *et al.*[15] assumes after Fink and Kessinger,[8] a sheath of thickness t with a constant order parameter over a normal bulk. A complex conductivity is assumed in the sheath, and the boundary-value problem is solved exactly in the *local, two-fluid classical* limit. At low κ the model fails before these last conditions are strongly violated because the model ignores depairing. For large κ Fink and Kessinger[8] have shown that $t \cong \xi$ in the entire sheath regime since, for $\kappa \gg 1$, $\xi \ll \lambda \cong \delta$, one has $t \ll \delta$. This thin sheath at H_{c2} does not contribute much absorption by depairing, but also it does not much attenuate the microwaves, which easily reach the normal bulk. With its short mean free path this bulk absorbs strongly, and therefore $R(H_{c2})$ is very large even though it is almost entirely dominated by carrier-motion absorption. Note that R_n is very large too. As κ becomes smaller, t at H_{c2} becomes larger. The contributions to absorption by depairing and carrier motion reverse in relative importance. At the same time, R_n decreases. When $\kappa \leq 1$, the sheath thickness at H_{c2} or H_c is very large ($t \gg \delta$) and absorption by carrier motion becomes negligible. To explain the persisting large ratio $R(H_c^+)/R_n$, one must assume absorption by depairing, and this, in turn, is possible only if the necessary depairing energy has been reduced by a large amount $2ev_FA_0/c$.

In conclusion, we believe that we have provided strong experimental evidence that a magnetic field reduces the observable optical energy gap (i.e., the energy necessary for depairing by electromagnetic radiation) at the free surface of a superconductor by a large linear term $2ev_FA_0/c$, and that we have explained the mechanism of this effect. We have also indicated in what sense the gaplessness in the excitation spectrum of the surface sheath is to be understood when κ is not very large.

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Indirect Coupling of Photons to the Surface Plasmon*

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Some mechanisms are investigated for the coupling of the surface plasma mode in a semi-infinite medium with a flat or almost flat surface to incident electromagnetic waves. In a classical approximation the mechanism of surface roughness (the departure of the surface from a perfectly flat, smooth plane) is studied. Using Green's-function techniques, the coupling of light to the surface plasmon assisted by phonons or impurities is considered. With phonons, the change in the reflectivity due to the mode may be on the verge of measurability at room temperature, while the change in reflectivity with coupling to an irregular surface or impurities near the surface is found to be measurable.

I. INTRODUCTION

In this paper some mechanisms are investigated for the coupling of the surface plasma mode in a semi-infinite metal to normally incident electromagnetic waves. Classically, direct coupling of light to the surface plasmon in a slab with perfectly smooth, flat surfaces occurs only in thin samples.[1] In this case the branch of the surface plasmon that describes "tangential" oscillations for small wave vectors couples to electromagnetic radiation if the incident electric field has a component of polarization parallel to the plane of incidence. The magnitude of this effect vanishes in thick samples as e^{-pd}, where d is the thickness of the slab and p is the wave vector of the mode parallel to the surface. Quantum mechanically the surface plasma mode in a thick sample possesses a small transverse component which couples to light when the electric field is polarized parallel to the plane of incidence.[2] However, this will contribute to the reflectivity only to order $(k/k_f)^2$, where k is the wave vector of light and k_f is the Fermi wave number. For light which strikes the surface at normal incidence, neither of the above mechanisms contribute to the reflectivity. In addition, Ritchie[3] has shown that the surface plasmon can couple to light through the intermediary of an intraband transition. This mechanism yields an absorption edge rather than a peak or resonance. The magnitude of this edge is not very large.

In this paper the coupling of the surface plasmon in a thick sample to normally incident light through surface irregularities,[4] phonons, and impurities is stud-

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[4] The coupling of the surface plasmon to light by means of roughness has been proposed as an explanation for the peak in radiation from surface plasmons produced by electrons incident very obliquely to Ag films by E. A. Stern, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland Publishing Co., Amsterdam, 1966), p. 397.

ied. The magnitude of the effect is characterized by the dimensionless quantity ΔR,

$$\Delta R = \omega_0^{-1} \int d\omega [R(\omega) - R_0(\omega)], \tag{1}$$

where $R(\omega)$ is the reflectivity of the metal as function of frequency, $R_0(\omega)$ is the reflectivity of the metal in the absence of the surface plasmon, and ω_0 is the resonant frequency of the surface plasmon. It is roughly estimated that ΔR can be of order 10^{-2} for Ag because of surface roughness or impurities near the surface. This brings the theory into rough agreement with the experiments of Jasperson and Schnatterly.[5] An accurate calculation would require a more detailed knowledge of the surface structure and a better knowledge of the structure of the surface plasmon for momenta which are not very small compared with the Fermi momentum. The coupling due to phonons contributes only about 10^{-3} to ΔR for Ag at room temperature.

The effects of a slightly rough surface on the surface plasmon are investigated classically in Sec. II. Instead of the perfectly smooth surface described by $z=0$, the surface in this section is defined by the equation

$$z + \sum_n a_n \sin(\mathbf{q}_n \cdot \boldsymbol{\rho} + \alpha_n) = 0, \tag{2}$$

where $\mathbf{q}_n$ is a wave vector in the x-y plane and cylindrical coordinates $\mathbf{r} = (\boldsymbol{\rho}, z)$ have been used. The surface plasma mode is studied to first order in the surface roughness components and it is found that the mode acquires a partially transverse character which allows it to couple to light.

In Sec. III (and the Appendix) the coupling of the surface plasmon in a semi-infinite metal to normally incident light through impurities and phonons is calculated using Green's-function techniques. A symmetric set of diagrams is used which yields the same bulk absorption as obtained by Hopfield[6,7] if one uses the random-phase-approximation (RPA) dielectric constant in his results. For phonons these diagrams describe the creation of a surface plasmon and phonon from an electron-hole pair excited by the incident light. The results of Secs. II and III are discussed in Sec. IV and are used to estimate ΔR for real metals. Since only impurities very close to the surface effect the excitation of surface plasmons, impurities are equivalent to surface roughness in many ways. The units used in the paper are cgs units with $\hbar = 1$.

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[6] J. J. Hopfield, Phys. Rev. **139**, A419 (1965).
[7] These diagrams also yield the expression for a quantum plasma obtained by A. Ron and N. Tzoar, Phys. Rev. **132**, 2800 (1963). The connection to our work can be seen by examining diagrams 4 and 5 in Fig. 1 of their work. In the quantum limit, the contribution to the conductivity from both electron-electron and electron-ion interactions comes when one wavy line represents screened electron–electron interactions only and the other wavy line represents screened electron–ion interactions.

II. SURFACE ROUGHNESS

The method used to investigate the effects of an irregular surface in this section is an extension of the method used by Ferrell[1] for perfectly smooth surfaces. The model consists of a metal characterized by the frequency dependency dielectric constant $\epsilon(\omega)$ below the surface defined by Eq. (2) and free space above that surface. The electric scalar potential ϕ satisfies Laplace's equation everywhere except at the surface in the absence of free charges. The normal modes of the system are obtained by finding the frequencies at which $\nabla \cdot \mathbf{D} = 0$ and $E \neq 0$.

Because of the irregular boundary, there is no convenient orthonormal set of functions to express ϕ in terms of. Instead it is convenient to solve Laplace's equation by transforming to a new coordinate system (denoted by the subscript zero) defined by

$$x_0 = x, \qquad y_0 = y,$$
$$z_0 = z + \sum_n a_n \sin(\mathbf{q}_n \cdot \boldsymbol{\rho} + \alpha_n)_0. \tag{3}$$

The sum in Eq. (3) includes components of surface roughness with wave vectors $\mathbf{q}_n$ in the x-y plane. These waves have amplitudes a_n and phases α_n. Because the new coordinate system is not orthogonal to the original one, ϕ is not the solution to Laplace's equation in the new system. Instead it satisfies the equation

$$[\nabla_0^2 + A(\mathbf{r}_0)]\phi(\mathbf{r}_0, t) = 0, \tag{4}$$

except at $z_0 = 0$. $A(\mathbf{r})$ is the operator,

$$A(\mathbf{r}_0) = \sum_{n,j} 2a_n q_{nj} \cos(\mathbf{q}_n \cdot \boldsymbol{\rho}_0 + \alpha_n) \partial^2/\partial z_0 \partial x_{0j} - \sum_{n,j} a_n q_{nj}^2 \sin(\mathbf{q}_n \cdot \boldsymbol{\rho}_0 + \alpha_n) \partial/\partial z_0 + \sum_j [\sum_n a_n q_{nj} \cos(\mathbf{q}_n \cdot \boldsymbol{\rho}_0 + \alpha_n)]^2 \partial^2/\partial z_0^2. \tag{5}$$

The index j takes on the values 1 and 2, where $x_1 = x$ and $x_2 = y$. The quantity q_{nj} is the jth component of $\mathbf{q}_n$. These last two equations are obtained from the Jacobian of the coordinate transformation described by Eq. (3).

Equation (4) can also be written in the integral form

$$\phi(\mathbf{r}_0, t) = \phi_0(\mathbf{r}_0, t) + \int d^3r' G(\mathbf{r}_0, \mathbf{r}') A(\mathbf{r}') \phi(\mathbf{r}'),$$

$$\nabla_0^2 G(\mathbf{r}_0, r') = -\delta^3(\mathbf{r}_0 - \mathbf{r}'),$$
$$\nabla_0^2 \phi_0(\mathbf{r}_0, t) = 0. \tag{6}$$

The quantity G is the Green's function for all space and its Fourier transform is $G(p) = p^{-2}$. The zero-order solution ϕ_0 solves the problem when $a_n = 0$ for all n. It is given by the equation

$$\phi_0(\mathbf{r}_0, t) = B \exp(-k|z_0| + i\mathbf{k} \cdot \boldsymbol{\rho}_0 - i\omega t),$$

where $\mathbf{k}$ is a wave vector in the x-y (x_0-y_0) plane, ω is the frequency of the mode, and B is an arbitrary coefficient. The solution for ϕ can be obtained by iterating Eq. (6) to any desired order. However, the second iteration is already horribly complicated and it appears feasible to iterate only once. For only one Fourier component of surface roughness additional iterations are less complex. However the inclusion of only one component of surface roughness is not very physical. To lowest order the resonant frequency is still given by $\epsilon(\omega)=-1$.

The last term of A, as defined by Eq. (5), is of order a^2 and is neglected since other terms from the second iteration are just as large. Thus only terms which are first order in a_n are kept. It is now straightforward to obtain the lowest-order solution for ϕ. After transforming back to the original coordinate system, the solution can be written as

$$\phi(\mathbf{r},t)=B\exp(-i\omega t)\{\exp(i\mathbf{k}\cdot\boldsymbol{\rho})\exp(-k\,|\,z_0\,|\,)+\epsilon(z_0)\sum_{n,\sigma}\exp[i(\mathbf{k}+\sigma\mathbf{q}_n)\cdot\boldsymbol{\rho}]C_{n\sigma}\times[\exp(-k\,|\,z_0\,|\,)-\exp(-k_{n\sigma}\,|\,z_0\,|\,)]\},\quad(7)$$

where z_0 is given by Eq. (3), $\epsilon(z)$ equals $+1$ if $z>0$ and -1 if $z<0$, and the quantity σ takes on the values ±1. The wave vector $\mathbf{k}$ is the wave vector of the unperturbed surface plasmon and the rest of the quantities are defined as

$$k_{n\sigma}=|\,\mathbf{k}+\sigma\mathbf{q}_n\,|,$$

$$C_{n\sigma}=-\tfrac{1}{2}ia_nk\sigma\exp(i\sigma\alpha_n).$$

In order to estimate the validity of the perturbation expansion, first consider only one component of surface roughness so that the surface is described by the equation $z+a\sin qy=0$. It is expected that the perturbation theory has some validity if the slope of the roughness is small, i.e., if aq is small compared to 1. This, and the condition that $aq^2<k$, guarantee that $|\,A\phi_0\,|<|\,\nabla_0{}^2\phi_0\,|$. In order that ϕ be a solution of Maxwell's equations, the electric displacement vector $\mathbf{D}$ derived from it must have a vanishing divergence everywhere. By another straightforward exercise one can verify that this occurs when $\epsilon(\omega)=-1$ only if $\mathbf{k}$ and $\mathbf{q}$ are parallel (or antiparallel) and $|\,k\,|\geq|\,q\,|$. However, for the absorption of normally incident light, only those modes for which $\mathbf{k}=\pm\mathbf{q}$ contribute. In order to make the divergence of $\mathbf{D}$ vanish otherwise, the B's for different values of $\mathbf{k}$ must be related.

When one combines various components of surface roughness the condition that the slope is small becomes

$$|\,\partial z_0/\partial x_j\,|<1.$$

What this implies about the a_n and q_n depends on the phased α_n. One might impose a sort of rms condition, that the quantity

$$\xi_j=[\sum_n(a_nq_{nj})^2]^{1/2}\qquad(8)$$

not be large. However, this may be a very poor approximation and, indeed, Eq. (3) may be a poor way to represent the surface of any metal. Nevertheless, it is within the spirit of this calculation to use some criterion such as Eq. (8) for the degree of the surface roughness. This point will be further discussed in Sec. IV. The fact that the B's should be coupled when more than one component of surface roughness is present has been neglected.

The contribution of the surface plasma mode to the normal incidence reflectivity of the sample is now calculated using first-order time-dependent perturbation theory. The effect of the roughness of the surface itself on the incident light is neglected since $(\omega a/c)^2$ is assumed to be very small compared to 1. (It is of order 10^{-6} if a is of the order of an atomic spacing and ω is near the surface plasma frequency in metals.) The interaction of the surface plasmon with an electromagnetic field is

$$H'=-c^{-1}\int\mathbf{A}\cdot\mathbf{J}d^3r,\qquad(9)$$

where $\mathbf{A}$ is the vector potential of the incident light in the gauge $\nabla\cdot\mathbf{A}=0$ and $\mathbf{J}$ is the current due to the surface plasmon. Since $\mathbf{J}=(\epsilon-1)\mathbf{E}/4\pi$ and $\mathbf{E}=-\nabla\phi$, one finds that the current in the x direction of a surface plasmon with original wave vector $\mathbf{k}$ is

$$J_x=(\omega B/2\pi)\exp(-i\omega t)\{k_x\exp[kz_0+i\mathbf{k}\cdot\boldsymbol{\rho}]+\sum_{n,\sigma}C_{n\sigma}(k+\sigma q_n)_x\exp[k_{n\sigma}z_0+i(\mathbf{k}+\sigma\mathbf{q}_n)\cdot\boldsymbol{\rho}]+\sum_{n,\sigma}[-C_n(k+\sigma q_n)_x-\tfrac{1}{2}ia_nq_{n,x}k\exp(i\sigma\alpha_n)]\times\exp[i(\mathbf{k}+\sigma\mathbf{q}_n)\cdot\boldsymbol{\rho}+kz_0]\}\quad(10)$$

for $z_0<0$ and zero for $z_0>0$.

The normally incident light is taken to be polarized in the x direction. A pulse of light is described by the vector potential

$$A(\mathbf{r},t)=\int d\omega\exp(-i\omega t)A(\omega)\exp(i\omega z/c),\qquad z>0$$
$$=\int d\omega\exp(-i\omega t)A(\omega)\exp(\omega z/c),\qquad z<0\qquad(11)$$

pointing in the x direction. Since the calculation is only for the lowest-order contribution to ΔR from the surface plasmon, the effect of the mode on A is neglected. The $A(\omega)$ is nonzero only in a small range around ω_0, the resonant frequency of the surface plasmon.

$$\omega_0=\omega_p/\sqrt{2}=ck_0.$$

The quantity k_0 is the wave number of the light, where c is the speed of light. It has been assumed that

$$\epsilon(\omega)=1-(\omega_p/\omega)^2, \tag{12}$$

where ω_p is the plasma frequency. Effects due to the imaginary part of $\epsilon(\omega)$ (such as the Drude tail) could be included as another perturbation. In fact in the present calculation the surface plasmon is arbitrarily narrow. This calculation does not obtain the mode's line shape but only its contribution as defined in Eq. (1) (a sort of "oscillator strength"). By first forming Poynting's vector one easily finds W, the incident energy of the pulse.

$$W=(2c)^{-1}L^2\omega_0^2\int d\omega\,|A(\omega)|^2, \tag{13}$$

for a sample enclosed in a square of side L in the x-y plane.

The energy from the incident pulse lost to the surface plasmon can be calculated by treating the surface plasmon as a harmonic oscillator.[1] The energy stored in the electric scalar field can easily be computed and is just $\frac{1}{2}$ of the total energy of the oscillator. To zeroth order in the roughness, this energy is

$$U_k=k\,|B|^2L^2/2\pi=n\omega_0, \tag{14}$$

where units with $\hbar=1$ are used. On the other hand, the energy transfer to the surface plasmon, ΔW, is

$$\Delta W=\omega_0\left|\int H'(t)\,dt\right|^2\Big/(n+1), \tag{15}$$

where the surface plasmon is excited to its nth state. Since the calculation is classical, $n\gg1$. From Eqs. (9), (10), (11), (14), and (15), one obtains

$$\Delta W=\omega_0^4\pi a_n^2 q_{nx}^2 L^2\,|A(\omega_0)|^2/2c^2k \tag{16}$$

as the contribution from the mode with wave vector $\mathbf{k}$, where $\mathbf{k}=\pm\mathbf{q}_n$. It has been assumed that $k_0\ll q_n$.

The reflectivity is the ratio of the power absorbed to the power reflected. Since the surface plasmon is arbitrarily narrow and

$$|A(\omega_0)|^2=\int d\omega\,|A(\omega)|^2\delta(\omega-\omega_0),$$

the total contribution to ΔR is

$$\Delta R=\sum_n 2\pi a_n^2 q_{nx}^2 k_0/|\mathbf{q}_n|. \tag{17}$$

The reason why ΔR is proportional to k_0 is that, except for extremely small wave numbers, the surface plasmon is localized in a distance much nearer the surface than the skin depth. Thus the surface plasma mode can take advantage of only a small part of the penetration of the electric field.

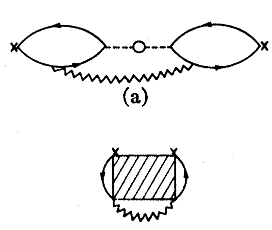

FIG. 1. One of the four diagrams contributing to the absorption: represented in different ways.

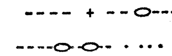

FIG. 2. The dynamically screened Coulomb potential.

III. IMPURITIES AND PHONONS

In this section the coupling of the surface plasmon to light through the intermediary of impurities or phonons is treated using the techniques of quantum field theory. The basic model is the interacting electron gas confined to a slab $0\leq z\leq d$ with perfectly smooth surfaces.[2] Some of the effects of bands can be added phenomenologically. The contribution from the surface plasma mode to α, the complex polarizability of the system, is calculated from a symmetric set of four diagrams. One of these diagrams is shown in Fig. 1, where the solid lines indicate single-particle propagators or Green's functions, the wavy line indicates a phonon or an interaction with an impurity, and the x's indicate the incoming and outgoing phonons. The dashed line with the circle represents the dynamically screened Coulomb interaction as shown in Fig. 2. The other three diagrams for α are the same except that the directions of the pairs of arrowheads on the bubbles are permuted. These diagrams yield the results obtained by Hopfield[6,7] for the bulk case if one uses the RPA dielectric constant in his result and the screened phonon interaction in ours.

Since in metals the frequency of the surface plasmon is much greater than any characteristic phonon frequency, the contribution to α from phonons and from impurities is similar. The calculation is carried out for impurities of concentration c and a screened potential. The mean free path for electron impurity scattering, l, can also be expressed in terms of these quantities and the final answer will depend only on l. The results are equally valid for phonons if l is taken to be the mean free path for electron–phonon scattering.

It is convenient to calculate separately the portion of the diagrams which includes the screened Coulomb interaction (and thus the surface plasma resonance) since it is the same for all four diagrams. This quantity is a correlation function which is called L and is shown

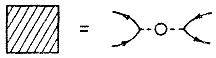

FIG. 3. The part of the diagrams that includes the surface plasma mode.

diagrammatically in Fig. 3 where it is represented by the shaded box. In terms of L, Fig. 1(a) becomes Fig. 1(b). That part of L which is due to the surface plasmon is calculated in the Appendix. The resonant frequency of the surface mode and its decay rate into the continuum depend linearly on p, the momentum of the mode parallel to the surface of the slab. Thus the mode will degenerate as p increases from zero and a cutoff is assumed to exist as some value q_c that is small enough so that an expansion in terms of (q_c/k_f) is reasonable. The subject of this cutoff is to be further discussed in Sec. IV.

Consider the case of normally incident radiation with the electric field polarized in the x direction. If the only absorption is due only to the surface plasmon, then

$$E(r,t)=E_0\exp(-i\omega t)\exp(ik_0z),\qquad z<0,$$
$$=E_0\exp(-i\omega t)\exp(-z/\delta),\qquad z>0,$$

where $\omega=ck_0$ and δ is the skin depth. The energy absorbed by the surface plasmon is

$$dw/dt=|E_0|^2\int\sigma_{xx}(r,\bar{r};\omega)\times\exp(-z/\delta)\exp(-\bar{z}/\delta)d^3rd^3\bar{r},\quad(18)$$

where the integrals extend over the range $0\leq z,\ \bar{z}\leq d$. The conductivity σ is given by the real part of $-i\omega\alpha$. After dividing by the incident flux, one obtains the reflectivity due to the mode.

$$R_s(\omega)=(4\pi\omega/c)\int\alpha''(z,\bar{z},\omega)\times\exp(-z/\delta)\exp(-\bar{z}/\delta)dzd\bar{z},\quad(19)$$

where α'' is the imaginary part of α and $\alpha(z,\bar{z},\omega)$ is equal to $\alpha(r,\bar{r},\omega)$ integrated over $\rho-\bar{\rho}$.

The part of α_{xx} (written as α from now on) represented by Fig. 1 is

$$\alpha_1(z_1z_2\omega)=-\frac{4e^2}{m^2\omega^2}\int dz_3dz_{3'}\int\frac{d^2p}{(2\pi)^2}\frac{d^2p'}{(2\pi)^2}\frac{d^2p''}{(2\pi)^2}\frac{d\omega'}{2\pi i}\frac{d\omega''}{2\pi i}(2d^7)^{-1}\sum(n_1+n_2+n_3+n_4)$$
$$\times G(\mathbf{p}'',k_1,\omega+\omega'')G(\mathbf{p}''+\mathbf{p},k_2,\omega'')G(\mathbf{p}'',k_6,\omega'')G(\mathbf{p}'+\mathbf{p},k_3,\omega'-\omega)$$
$$\times G(\mathbf{p}',k_4,\omega')G(\mathbf{p}',k_5,\omega'-\omega)p_x'p_x''|u(\mathbf{p},k_7)|^2\,cn[\bar{L}(\mathbf{p}\omega,k_1k_2k_3k_4)]$$
$$\times\sin k_1z_1\sin k_6z_1\sin k_4z_2\sin k_5z_2\sin k_2z_3\sin k_6z_3\cos k_7(z_3-z_{3'})\sin k_3z_{3'}\sin k_5z_{3'},\quad(20)$$

where the summation is over k_1 through k_7 and the z integrations extend from 0 to d. The impurities are characterized by their concentration c and potential $u(q)$ while n is the density of electrons. The rest of the quantities are defined in the Appendix. The contributions from the other three diagrams are similar.

To a very good approximation, the integral in Eq. (19) is given by

$$\alpha(\omega)=\frac{1}{4}\int dzd\bar{z}\,\alpha(z,\bar{z};\omega),\quad(21)$$

where the z integrals run from zero to d. The reason is that $1/\delta$ is much less than any characteristic momentum in the system (such as q_c and k_f). In other words, the electromagnetic field penetrates much further into the metal than the surface plasmon does. The factor of $\frac{1}{4}$ comes from the fact that only one surface is exposed to the light. This approximation may also be verified by a direct integration of α. After adding the contributions from the other diagrams and performing the ω and z integrations, one obtains

$$\alpha_s(\omega)=-\frac{e^2}{m^2\omega^4}\int\frac{d^2p}{(2\pi)^2}\frac{d^2p'}{(2\pi)^2}\frac{d^2p''}{(2\pi)^2}(2d^5)^{-1}\sum\{n_1+n_2+n_3+n_4\}\,cnp_x^2$$
$$\times|u(\mathbf{p},k_7)|^2\bar{L}_s(\mathbf{p}\omega,k_1k_2k_3k_4)\big(d\delta(k_7+k_2-k_1)d\delta(k_7+k_3-k_4)$$
$$+4k_7^2[(k_3+k_4)^2-k_7^2]^{-1}[(k_1+k_2)^2-k_7^2]^{-1}\{n_3+n_4+n_7+1\}\{n_1+n_2+n_7+1\}\big)\delta(E(\mathbf{p}'',k_1))\delta(E(\mathbf{p}',k_3)),\quad(22)$$

where the summation is over n_1, n_2, n_3, n_4, and n_7. This is the contribution to $\alpha(\omega)$ from the surface plasmon as discussed in the Appendix.

After substituting $\bar{L}_s$ in the equation from Eq. (A10), one can perform the n_3 and n_4 sums. Then using the fact that

$$(2d)^{-1}\sum_n f(k_n)\underset{d\to\infty}{\longrightarrow}\int\frac{dk}{2\pi}f(k),$$

one obtains

$$\alpha_s(\omega)=\frac{4e^4k^2{}_f}{\pi^3\omega^4}\int\frac{d^3q}{(2\pi)^3}\,u^2(q)\,\frac{q_\perp}{q^2}\,\mathrm{cn}\,\frac{[1-\epsilon(\omega)]^2}{8\epsilon(\omega)D(\omega_2q_\perp)}\,,\quad(23)$$

where $q_\perp=(q_x^2+q_y^2)^{1/2}$.

Since this is the contribution from the surface plasmon, set $\epsilon(\omega)=-1$. The integration in Eq. (23) is now performed with a cutoff in the $q_\perp$ integration at q_c. Terms of order (q_c/k_f) are neglected. The concentration c is expressed in terms of the mean free path for electron-impurity scattering l under the assumption that $u(q)$ is a screened potential with a screening momentum of approximately k_f. Then, after integrating over ω, one uses Eqs. (1), (19), and (23) to obtain

$$\Delta R=k_0q_c^2(\omega_p^*/\omega_0)^4 3\pi^2/2k_f^4l,\qquad(24)$$

$$(\omega_p^*)^2=4\pi ne^2/m,\qquad(25)$$

where n is the density of electrons and ω_0 is the resonant frequency of the surface plasma. ω_p^* is not necessarily the observed plasma frequency. The quantity k_0 is the wave number of the incident light,

$$\omega_0=ck_0,$$

where c is the speed of light. The effect on the reflectivity due to the surface plasmon obtained from Eq. (23) is

$$R(\omega)-R_0(\omega)=(3\pi k_0\omega_0g/2v_s^2k_f^4l)\,(\omega_p^*/\omega_0)^4$$
$$\{\tfrac{1}{2}\ln[((\omega_0+v_sq_c-\omega)^2+g^2)/((\omega-\omega_0)^2+g^2)]$$
$$-\tan^{-1}((\omega_0+v_sq_c-\omega)/g)+\tan^{-1}((\omega_0-\omega)/g))\},$$

where the surface plasmon frequency is $\omega_0+v_sq_\perp$ and the momentum dependence of the decay rate is neglected with respect to g, the intrinsic decay rate which is independent of $q_\perp$.

IV. DISCUSSION

The surface plasma mode has arbitrarily been cut off at the momentum (or wave number) q_c. The contribution to the reflectivity from phonons or impurities depends on the square of this quantity. The quantity ΔR due to surface roughness must also depend on this quantity since the sum in Eq. (17) must be restricted to values of n such that $|q_n|<q_c$. For a summation over many components of surface roughness, the sum may also depend on q_c^2. The mode becomes broader and more degraded as p, the momentum of the mode parallel to the surface, increases because both the dispersion and decay rate increase linearly[2] with p for $p\ll k_f$. The behavior of the mode for p not much less than k_f is not known and the cutoff is introduced as a convenience. Thus the quantity is not terribly well defined and any value we choose for it is somewhat arbitrary. Also, the shape of the line should not pe Lorentzian since the quantity D in the denominator of the integrand in Eq. (23) actually contains these real and imaginary terms depending on $q_\perp$.

In order to estimate numbers for Ag a value of $q_c=0.3k_f$ is chosen[8] and, of course, the results are uncertain to the extent that they depend on q_c. Since silver has a density of about 5.8×10^{22} cm^{-3} its Fermi momentum in the free-electron model is 1.2×10^8 cm^{-1} and ω_p^* is 8.5 eV. The unshifted surface plasma frequency ω_0 is about 3.4 eV.

The contribution from the surface plasmon to the reflectivity through the coupling of surface roughness is given by Eq. (17). For only one component of surface roughness the contribution to the reflectivity for light polarized along that component is

$$\Delta R=2\pi a^2qk_0.$$

If a is of order $(1/k_f)$ and $q\sim q_c$, this gives $\Delta R\sim3\times10^{-3}$ for Ag. However, the only restriction that was placed on a was that $aq<1$. For aq equal to one and $q\sim q_c$, one obtains $\Delta R\sim3\times10^{-2}$. These numbers give the order of magnitude that one might expect for ΔR under somewhat favorable conditions of surface roughness.

In order to describe a surface realistically, one probably has to take into account a large number of surface components. Another crude estimate of ΔR can be generated by taking a large number N of surface components along the x direction and spacing them equally so that

$$q_n=n\gamma k_f/N,\qquad(26)$$

where n runs from 1 to N and γk_f is the maximum wave number of the components. Further, assume that all a_n are equal and that the sum in Eq. (17) is restricted to $q_n<q_c$. The quantity ξ given by Eq. (8) is taken to be the measure of surface roughness. From Eqs. (8), (17), and (26), one obtains

$$\Delta R=(3\pi\xi^2/\gamma^3)(k_0q_c^2/k_f^3).\qquad(27)$$

For $\xi=1$ and $\gamma=\frac{1}{2}$, this yields $\Delta R\sim10^{-2}$ for Ag. It is quite sensitive to the values of γ and q_c.

Equation (24) gives the contribution to the reflectivity from the surface plasmon due to impurities or phonons. Any number obtained from it is uncertain to the extent that it depends on q_c^2. For Ag, with $q_c=0.3k_f$, one obtains

$$\Delta R\sim0.2/lk_f.\qquad(28)$$

For phonons at room temperature $\Delta R\sim10^{-3}$.

Since only the properties within a few atomic spacing really determine ΔR, the relevant mean free path for the electrons is the mean free path very near the surface. In other words, only the concentration of impurities near the surface contributes to $\alpha(\omega)$ as defined

[8] A value for q_c of about $0.5k_f$ has been measured for surface plasmons in alkali halides by electron energy loss experiments by O. Sueoka, J. Phys. Soc. Japan **20**, 2226 (1965).

by Eq. (21). Thus l can be thought of as the mean free path due to surface impurities and irregularities. In other words as far as the surface plasmon is concerned, there is little difference between impurities and surface roughness and, indeed, impurities very near the surface are a form of surface roughness. If the first few atomic layers of a surface were doped with impurities, the surface plasma absorption would be enhanced with very little change in the bulk optical properties. Of course as the doping increases the surface plasmon becomes more degraded. However, for a concentration of impurities near the surface such that the imaginary part of the bulk dielectric constant would not be greatly changed with the same concentration of impurities in the bulk, the width of the resonance would probably remain unchanged. By controlling the doping, and thus l, a determination of an effective q_c might be made.

The quantity ΔR can be brought into agreement with the data of Jasperson and Schnatterly,[4] who find $\Delta R \sim 10^{-2}$, by choosing l, due to impurities near the surface, equal to 20 Å. However, because of the dependence on q_c^2, the same answer could be obtained for $l = 80$ Å if q_c were $0.6k_f$. In addition, the maximum value of $R(\omega) - R_0(\omega)$ given by Eq. (2.6) is about 0.03 if v_s is of order ω_0/k_f, $q_c \sim 0.3k_f$, and g, as determined from measurements of $\epsilon_2(\omega)$, is about $0.1\omega_0$. This, and the slightly non-Lorentzian line shape expressed by Eq. (2.5), are compatible with the measurements of Jasperson and Schnatterly[4] on some samples.

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APPENDIX

In this Appendix a brief derivation is sketched for the correlation function L used in Sec. III, which is shown diagramatically in Fig. 3. The techniques used to deal with the surface and derivation of the single-particle Green's functions are obtained from Ref. 2. The single-particle Green's[9] function is defined as

$$G(11') = -i\langle T[\psi(1)\psi^+(1')]\rangle, \qquad \text{(A1)}$$

whose arguments n stand for the space-time coordinates $(\mathbf{r}_n, t_n)$. The symbol T indicates time ordering and the angular bracket $\langle x\rangle$ means that the expectation value at zero temperature is taken. ψ^+ and ψ are the electron creation and destruction operators. From Eq. (A2) of Ref. 2, the Green's function is obtained:

$$G(\mathbf{r}\mathbf{r}', t-t') = \int \frac{d\omega}{2\pi} \int \frac{d^2p}{(2\pi)^2} d^{-1} \sum_n \exp[i\omega(t-t')] \times \exp i\mathbf{p}(\boldsymbol{\rho}-\boldsymbol{\rho}') \sin kz \sin kz' [G(\mathbf{p}, k, \omega)],$$
$$G(\mathbf{p}, k, \omega) = [\omega - E(\mathbf{p}, k) + i\delta \operatorname{sgn}(|q| - q_f)]^{-1}, \qquad \text{(A2)}$$

where δ is a vanishingly small positive quantity and q_f is the Fermi momentum. The values of k are $n\pi/d$ and the cylindrical coordinates $(\mathbf{r} = \boldsymbol{\rho}, z)$ and $\mathbf{q} = (\mathbf{p}, k)$ are used. The single-particle energy $E(q)$, given by $(q^2 - q_f^2)/2m$, is measured from the Fermi surface.

The integral equation for L is

$$L(11', 22') = \int d3d4 G(13)G(31')v(34)G(24)G(42') - 2i \int d3d4 G(13)G(31')v(34)L(44, 22'), \qquad \text{(A3)}$$

where $v(34)$ is the Coulomb potential multiplied by a delta function in time and dn denotes the space-time integration $d^3r_n dt_n$. In order to obtain $L(11', 22')$, one must first obtain $L(11, 22')$, which satisfies the equation $L(11, 22') = L'(1, 22')$

$$= \int d3d4 G(13)G(31)v(34)G(24)G(42') - 2i \int d3d4 G(13)G(31)v(34)L'(4, 22'). \qquad \text{(A4)}$$

In order to solve this equation, $\bar{L}$ is Fourier transformed according to the prescription

$$L'(1, 22') = \int \frac{d^2p}{(2\pi)^2} \int \frac{d^2p'}{(2\pi)^2} \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} \frac{1}{d^3} \sum_{n,n',n''} \{n+n'+n''\} L'(\mathbf{p}\omega, \mathbf{p}'\omega', kk'k'') \exp[-i\omega(t_1-t_2) - i\omega'(t_2-t_{2'}) + i\mathbf{p}\cdot(\boldsymbol{\rho}_1-\boldsymbol{\rho}_2) + i\mathbf{p}'\cdot(\boldsymbol{\rho}_2-\boldsymbol{\rho}_{2'})] \cos kz_1 \sin k'z_2 \sin k''z_{2'}, \qquad \text{(A5)}$$

where the curly brackets $\{n\}$ restrict the summation to even values of n. As in Ref. 2, the method of obtaining $\bar{L}$ is straightforward but tedious. It is somewhat simplified here because only the limit $pd \to \infty$ is being considered.

The solution for L' is

$$L'(\mathbf{p}\omega, \mathbf{p}'\omega', kk'k'') = iG(\mathbf{p}'-\mathbf{p}, k', \omega'-\omega)G(\mathbf{p}', k'', \omega')\bar{L}(\mathbf{p}\omega, kk'k''), \qquad \text{(A6)}$$

[9] The definition of G and its Fourier transform in time is the same as that used for zero temperature in A. A. Abrikosov, L. P. Gorkov, and I. E. Dzaloshinski, *Methods of Quantum Field Theory in Statistical Mechanics*, translated by R. A. Silverman (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

where $\bar{L}$ is the solution to the equation

$$\bar{L}(kk'k'')=[\{B(k)v(k)(d/8)[\delta(k+k'-k'')+\delta(k-k'+k'')]$$
$$-\tfrac{1}{2}v(k'-k'')[B(k)p(p^2+k^2)^{-1}-C(k)+\tfrac{1}{4}B(\tfrac{1}{2}(k-k'+k''),\tfrac{1}{2}(k+k'-k''))+\tfrac{1}{4}B(\tfrac{1}{2}(k+k'-k''),\tfrac{1}{2}(k-k'+k''))]\}$$
$$-\{\text{same with } k''\to -k''\}-2R(kk'k'')-2C(k)S(k'k'')-2S(k'k'')B(k)p(p^2+k^2)^{-1}](1-2B(k)v(k))^{-1}, \quad \text{(A7)}$$

where the $\mathbf{p}$ and ω dependence of the quantities have been suppressed where possible, and where

$$S(k'k'')=d^{-1}\sum_{n}\bar{L}(kk'k'')v(k)\{n+n'+n''\},$$
$$v(k)=4\pi e^2/(p^2+k^2),$$
$$R(kk'k'')=(2d)^{-1}\sum_{n}B(\bar{k},\bar{k}+k)v(2\bar{k}+k)\bar{L}(2\bar{k}+k,k',k''),$$
$$C(k)=(2d)^{-1}\sum_{n'}B(k',k'+k)p[p^2+(2k'+k)^2]^{-1},$$
$$B(k)=(2d)^{-1}\sum_{n'}B(k'+k,k'), \quad \text{(A8)}$$

and

$$B(k_1k_2)=\int\frac{d^2p'}{(2\pi)^2}\frac{f(\mathbf{p}+\mathbf{p}',k_1)-f(\mathbf{p}',k_2)}{E(\mathbf{p}'+\mathbf{p},k_1)-E(\mathbf{p}',k_2)-\omega-i\delta},$$

with $f(\mathbf{p},k)=f(\mathbf{q})$ the Fermi factor which equals 1 for $q<q_f$ and zero for $q>q_f$.

Since the surface plasma resonance is cutoff at a value of p small compared to k_f, it is sufficient to solve these equations to lowest order in (p/k_f). They are also solved only for $|k|$ and $|k'\pm k''|$ small compared to k_f since this will give the largest contribution. The surface plasma resonance is contained in the function S. To lowest order, the only parts of $\bar{L}$ that contributes to the determination of S given by Eq. (A8) are the term with the Kronecker delta, the term $vBp[p^2+k^2]^{-1}$, and the term $-2SBp(p^2+k^2)^{-1}$ in Eq. (A7). Using these, one obtains

$$S(k'k'')=[1-\epsilon(\omega)][v(k'-k'')-v(k'+k'')]\tfrac{1}{4}[1+\epsilon(\omega)]^{-1}, \quad \text{(A9)}$$

where $\epsilon(\omega)$ is given by Eq. (12). The quantity $B(q)v(q)=\frac{1}{2}(1-\epsilon)$ and the wave number dependence of ϵ has been neglected. R contributes only to higher order so

$$\bar{L}_s(kk'k'')=\tfrac{1}{8}[1-\epsilon(\omega)][v(k'-k'')-v(k'+k'')]\epsilon^{-1}(\omega)[1+\epsilon(\omega)]^{-1}. \quad \text{(A10)}$$

The subscript s denotes that this is the lowest-order part of $\bar{L}$ that contains the surface plasma resonance.

Now L is Fourier transformed according to the prescription

$$L(11',22')=\int\left[\prod_{i=1}\frac{d^2p_1d\omega_1}{(2\pi)^3}\right]\frac{1}{d^4}$$
$$\times\sum\{n_1+n_2+n_3+n_4\}L(\mathbf{p}_1\omega_1,\mathbf{p}_2\omega_2,\mathbf{p}_3\omega_3',k_1k_2k_3k_4)$$
$$\times\exp[-i\omega_1(t_1-t_{1'})-i\omega_2(t_1-t_2)-i\omega_3(t_2-t_{2'})$$
$$+i\mathbf{p}_1\cdot(\boldsymbol{\varrho}_1-\boldsymbol{\varrho}_{1'})+i\mathbf{p}_2\cdot(\boldsymbol{\varrho}_1-\boldsymbol{\varrho}_2)+i\mathbf{p}_3\cdot(\boldsymbol{\varrho}_2-\boldsymbol{\varrho}_{2'})]$$
$$\times\sin k_1z_1\sin k_2z_{1'}\sin k_3z_2\sin k_4z_{2'}, \quad \text{(A11)}$$

where the summation is over n_1, n_2, n_3, n_4. The quantity L can easily be obtained from L' through Eq. (A4). Since only the surface plasmon part is of interest, the first term on the right-hand side of Eq. (A4) is irrelevant. To lowest order, one obtains

$$L_s(\mathbf{p}_1\omega_1\mathbf{p}\omega\mathbf{p}_2\omega_2,k_1k_2k_3k_4)$$
$$=G(\mathbf{p}+\mathbf{p}_1,k_1,\omega+\omega_1)G(\mathbf{p}_1,k_2,\omega_1)$$
$$\times G(\mathbf{p}_2-\mathbf{p},k_3,\omega_2-\omega)G(\mathbf{p}_2,k_4,\omega_2)\bar{L}_s(k_1k_2k_3k_4),$$
$$\bar{L}_s(k_1,k_2,k_3,k_4)=[1-\epsilon(\omega)]^2p[-8\epsilon(\omega)D(\omega)4\pi e^2]^{-1}$$
$$\times[v(k_1-k_2)-v(k_1+k_2)][v(k_3-k_4)-v(k_3+k_4)], \quad \text{(A12)}$$

for the contribution to L from the surface plasmon.

The quantity D is the factor which contains the surface plasma resonance. If the wave-number dependence of the mode is neglected, $D(\omega)$ is given by

$$D(\omega)=1+\epsilon(\omega).$$

Actually D contains real and imaginary parts proportional to $(p_x^2+p_y^2)^{1/2}$.