Surface Plasma Oscillations of a Degenerate Electron Gas*

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Following Ritchie, the anomalous characteristic energy losses of energy lower than the plasmon energy, exhibited by some metals, are attributed to quantized surface waves of the degenerate electron gas. Although Ritchie's theory has been verified for an ideal pure metal surface by Powell and Swan by reflection of high-energy electrons, the transmission experiments show a lower energy loss generally. This is accounted for by taking into account the relaxation produced by the oxide coating on the surface of the metal. In this way, the experimental data is completely accounted for without the assumption of any anomalous bulk dielectric properties of the metal. The present paper studies the dependence on thickness of the oxide coating, and it is found that a surprisingly thin coating, say only 20 angstroms thick, can produce a significant effect. It is established that a measurement of the dispersion of the energy loss versus angle of scattering in the transmission experiment would yield a measurement of the oxide film thickness. A further check on the theory is suggested by a measurement of the angular dependence of the intensity of the low-lying characteristic energy loss. A special effect is predicted for non-normally incident fast electrons. It should be found that the intensity pattern should flare away from the plane of incidence. Besides these special angular effects it is predicted that because of the sensitivity of the surface plasma oscillations to any surface coating the value of the surface characteristic energy loss can be varied between wide limits by choosing the appropriate coating. In particular, making double films of two different metals should produce surface characteristic energy losses in between the bulk characteristic energy losses of the two separate metals.

I. INTRODUCTION

RITCHIE[1] has noted for a semi-infinite plasma that there exists not only the bulk plasma oscillations of the classical frequency ω_p in the interior of the plasma, but also surface plasma oscillations, the quanta of which we will call surface plasmons, at the interface between the plasma and vacuum of a frequency $\omega_p/\sqrt{2}$. He has further estimated the excitation probability of these modes of oscillation and has found that they should be quite observable in the usual characteristic energy loss experiments of fast electrons impinging upon metal samples, if the metal does not deviate significantly from the ideal behavior of a free electron gas. Various metals seem to satisfy this condition, in particular aluminum, in which it is well established that the bulk plasma frequency is approximately equal to that given by the classical formula, with very little absorption, as indicated by the very small linewidth. A further reason for believing that the surface waves should be detectable in an ideal metal such as aluminum is given by the fact that Fano,[2] following the suggestion of Rayleigh,[2] has been able to account for the anomalous diffraction patterns of gratings by essentially these same modes of vibration of the electrons in the aluminum composing the gratings. A further reason for believing that the surface plasma oscillations should exist is that Gould and Trivelpiece[3] have been able to establish their existence in gaseous plasmas by means of microwave techniques. It is therefore quite gratifying that Powell and Swan[4] have been able to detect the excitation of surface plasma oscillations in both aluminum and in magnesium by reflection of fast incident electrons, at energies close to those predicted by Ritchie. But the more conventional technique of characteristic energy loss measurements, involving the transmission of the incident electrons through the metal film, has always yielded significantly lower energy for the low-lying characteristic energy losses, and often a weaker intensity than predicted.[5] It has also been found by the experimentalists that the low-lying characteristic energy losses are very sensitive to sample preparation and can differ considerable from one film to another.[6] This behavior found in the transmission experiments has been explained by one of the authors in terms of the relaxation in the surface plasmon frequency produced by the oxide coating at the metal surface.[7] The oxide coating can be expected to cause the surface plasmon line at the bulk plasma frequency divided by the square root of two to be smeared out and to disappear, and to produce a new line at the bulk frequency divided by the square root of one plus the dielectric constant of the oxide. Recently, Powell and Swan[8] have succeeded in verifying this behavior for both aluminum and magnesium, under closely controlled conditions in which the metallic surfaces permitted to oxidize while under observation, while Wagner, Marton, and Simpson[8] have also more recently verified this behavior for aluminum. The purpose of the present paper is to present the quanti-

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[6] L. Leder, J. A. Simpson and L. Marton (private communication).

[7] E. A. Stern, Bull. Am. Phys. Soc. **4**, 235 (1959).

[8] C. J. Powell and J. B. Swan, Phys. Rev. **118**, 640 (1960); M. D. Wagner, L. Marton, and J. Arol Simpson, Bull. Am. Phys. Soc. **5**, 68 (1960).

tative theory of the effect of the oxide coating, and in particular to study in detail the dependence of the characteristic energy loss on the thickness of the oxide coating. The main result of the work is to establish the somewhat surprising conclusion that a very thin coating of only a few angstroms, say 20 for 10 kev and even thinner coatings for lower energy electrons, is already very effective in causing the ideal characteristic energy loss for a pure surface to disappear, and in causing to appear instead the relaxed characteristic energy loss with an appreciable intensity at a significantly lower energy.

The present investigation makes it abundantly clear that it would be highly desirable to have more advanced transmission experiments made in which the angular dependence of the low-lying characteristic energy loss were studied. The measurement of the dependence of the loss energy upon angle of scattering of the incident electron would yield a determination of the thickness of the oxide coating. The measurement of the variation of the intensity as a function of angle would, in addition, give a check on the theory of the surface oscillations. Such angular measurements, although difficult, do not seem to be impossible with present techniques. Further experiments to test the basic feature of the surface oscillations can take advantage of the dependence of the frequency of oscillation on the media surrounding the metal films. For example, a double film composed of a layer of aluminum and a layer of magnesium would give a surface plasma oscillation with a new quantum energy of about 13 electron volts.

Section II consists in a treatment of the surface oscillations possible for a semi-infinite degenerate electron gas bounded by a different semi-infinite dielectric medium. In this section, we derive by a different method from that used by Ritchie the formula for the differential cross section for the excitation of a surface oscillation in the transmission experiment and thereby generalize Ritchie's formula for the case of a dielectric medium instead of a vacuum and also for the case of non-normal incidence. It is found in the latter case that there should exist a characteristic flaring of the intensity pattern away from the plane of incidence. Section III studies the more complicated case of a dielectric medium of finite thickness bounding the plasma and beyond which there exists vacuum. Special attention is given to the dependence of the characteristic energy loss on the thickness of the dielectric layer. Section IV constitutes a brief conclusion.

II. SURFACE WAVES

In this section we study the case of a semi-infinite degenerate electron gas bounded by a semi-infinite ideally nonabsorptive dielectric medium. We assume that the electron gas can be described by the ideal plasma dielectric constant, which as a function of frequency has the form

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

where ω is the angular frequency, and ω_p is the classical plasma frequency, given by the standard formula

$$\omega_p=(4\pi ne^2/m)^{\frac{1}{2}}. \tag{2}$$

m, e, and n are the electron mass, charge, and number density, respectively. We attempt to find nontrivial solutions when no external charges are present. The electric scalar potential distribution set up by a classical charge wave bound to the surface, and traveling parallel to it, must decrease to zero at infinite distance from the interface, and must satisfy Laplace's equation within the metal and the dielectric medium. It therefore must have the form

$$\varphi(x,z,t)=2\varphi_0\cos(kx-\omega t)e^{-k|z|}, \tag{3}$$

where $2\varphi_0$ is the amplitude of the running wave, k is its wave number, and we are using Cartesian coordinates x and y parallel to the surface and z normal to it. It is then easy to see that the charge density at the interface given by $-\nabla^2\varphi/4\pi$ is

$$\rho(x,z,t)=(k\varphi_0/\pi)\cos(kx-\omega t)\delta(z), \tag{4}$$

where $\delta(z)$ is the Dirac delta function. This charge consists of the polarization charge of the dielectric plus the electric charge from the plasma electrons. From the condition that the normal component of the electric displacement vector should be continuous in passing across the interface from the electron gas into the dielectric medium, we have the equation

$$\epsilon_p(\omega)=-\epsilon, \tag{5}$$

where ϵ is the dielectric constant of the bounding medium. If we assume that ϵ is frequency independent, which will be a satisfactory enough assumption for dielectric layers on metal surfaces, we find upon substituting from Eq. (1) the resonant frequency for the surface wave of

$$\omega_r=\omega_p/(1+\epsilon)^{\frac{1}{2}}. \tag{6a}$$

For a plasma bounded by vacuum we must set $\epsilon=1$ and we obtain just Ritchie's[1] result. But if ϵ is significantly greater than 1 for an actual dielectric medium, then we find a significant relaxation in the resonant frequency given by Eq. (6a). It is just this effect which accounts for the difference between the experiments of Powell and Swan on perfectly clean metallic surfaces, and the usual results of the transmission experiments on metal films which have been permitted to oxidize.[7] It should be noted at this point that there will not necessarily be a sharp resonant frequency at the value given by Eq. (6a), since it may very well happen in actual cases that the dielectric medium is strongly absorptive at this frequency. If that is the case then it has in addition to

a real part of the dielectric constant ϵ_r an imaginary part ϵ_i, and the resonant frequency is no longer real but complex, though still given by Eq. (6a). For small values of ϵ_i we can extract the imaginary part of the resonant frequency, which gives in turn the lifetime τ, or the breadth of the resonance τ^{-1}, according to the following equation:

$$\tau^{-1}=2\omega_i=\omega_r\epsilon_i/(1+\epsilon_r)^{\frac{3}{2}}. \tag{6b}$$

Although this equation is valid only for small values of ϵ_i it nevertheless indicates that when ϵ_i approaches and exceeds unity the breadth of the line becomes of the same order of magnitude as the resonant frequency and that one can no longer speak of a collective oscillation. In this case one would not observe a distinct characteristic energy loss but instead a smeared-out continuum distribution which would, no doubt, evade detection. For this reason it is clear that the surface plasma oscillations in the presence of a bounding dielectric medium such as a metallic oxide are not necessarily observable but depend upon the actual dielectric properties of the bounding medium. In some cases, the resonant frequency will fall in the nonabsorbing region of the medium, and it is to these cases that we address ourselves in this paper.

Before proceeding further it is worthwhile first to point out an interesting possibility which arises because of Eq. (5) for the case of two plasmas of two different electron densities bounding one another. In that case we can let ϵ be of the same form as ϵ_p but with a different plasma frequency, say ω_p'. In this case, ϵ is no longer frequency independent and the solution given by Eq. (6a) no longer holds. Instead we find for the resonant frequency of the plasma wave along the metal-metal interface the value

$$\omega=[\tfrac{1}{2}(\omega_p^2+\omega_p'^2)]^{\frac{1}{2}}. \tag{7}$$

As a particular example we may imagine a double film made up of a layer of aluminum followed by a layer of magnesium. In this case, if we take as values for $\hbar\omega_p$ and $\hbar\omega_p'$ the values 15.3 ev and 10.6 ev found by Powell and Swan[4] for aluminum and magnesium, we find for $\hbar\omega$ the value 13.1 ev. The detection of a characteristic energy loss at this energy for such a double aluminum magnesium film would be further strong evidence of the validity of the surface wave interpretation of the low-lying characteristic energy losses.

Let us now return to the cases of pure aluminum and pure magnesium bounded by their own oxides. In these cases, Powell and Swan[8] find that the surface plasmon relaxes from 10.3 ev to 7.1 ev for aluminum and from 7.1 ev to 4.9 ev for magnesium. In each case, in order to interpret this result we must according to Eq. (6a) ascribe to the dielectric constant the value $\epsilon=3.65$. (The same value for both cases.) This corresponds to an index of refraction for these oxides of $N=\sqrt{\epsilon}=1.91$, which can be compared with the Handbook[9] values of 1.76 and 1.74, for sodium light. Although there are no published ultra-violet measurements of the index of refraction for these oxides, the dispersion in the visible range indicates that it is not unreasonable to expect such a rise of about ten percent in the index of refraction. It is further evident that the relaxed frequency for the surface waves falls below the threshold for absorption by the oxides. As explained above, this would not *a priori* necessarily be the case, for in general it can happen that the oxide will cause the disappearance of the original plasma vacuum line, without causing the reappearance of a relaxed line to take its place.

In order to describe in more detail the excitation of the surface waves it is necessary to compute the probability of scattering an incident electron by an angle θ, corresponding to a momentum recoil along the surface of $\hbar k$. The scattering coefficient will be computed according to a semiclassical method already published,[10] which will therefore be described here only very briefly. We consider the perturbation of the classical wave of Eq. (3) on an incident electron quantized in the volume V which encloses the metal film which can be considered to have the area A. The perturbation on the incident electron is time dependent and we are interested here only in the coefficient of the function $\exp(i\omega t)$, which causes the incident electron to lose energy. The coefficient of this function is

$$H'=-e\varphi_0 e^{-k(ix+|z|)}, \tag{8}$$

whose matrix element is to be taken between initial and final plane waves of the incident electron. This can be calculated straightforwardly or by the following trick. Since H' can be considered as a potential acting upon the electron the matrix element can be considered as the energy of interaction of H' with the transition charge density of the electron. But by the reciprocity of the Coulomb interaction we can consider that the incident electron in making its transition sets up the effective electric scalar potential

$$\varphi_{\text{eff}}=-(4\pi e/V)[k^2+(\Delta k)^2]^{-1}e^{i(kx+\Delta kz)}, \tag{9}$$

where Δk is the momentum transfer normal to the foil. Consequently, the matrix element we desire is the integral of this φ_{eff} with the charge density corresponding to H'. This charge density is in turn the coefficient of the right-hand member of Eq. (4) of the function $\exp(i\omega t)$. Consequently, we find for the matrix element in question the expression

$$\langle H'\rangle=-e\varphi_0\frac{A}{V}\frac{2k}{k^2+(\Delta k)^2}. \tag{10}$$

[9] *Handbook of Chemistry and Physics*, edited by C. D. Hodgman (Chemical Rubber Publishing Company, Cleveland, Ohio, 1958–59), 40th ed., pp. 526 and 602.

[10] R. A. Ferrell, Phys. Rev. **111**, 1214 (1958).

This is a matrix element for the scattering by the classical surface wave, although it is the same as by the plasma in a high quantum state. We can determine the degree of excitation by evaluating the energy per unit area of interface U, which is given by twice the electrostatic energy per unit area of interface. (This is most easily seen by considering the running wave to be a superposition of two standing waves.) Thus we have to compute the self energy of interaction of the portion of the charge density produced by the bunching of the plasma electrons at the surface, ρ_p, with the potential which it sets up. Since ρ_p differs from ρ of Eq. (4) by the factor $(1+\epsilon)/2$, we find

$$\frac{U}{2}=2A^{-1}\int\rho_p\varphi dxdydz$$
$$=[(1+\epsilon)/4\pi]k\varphi_0^2. \tag{11}$$

The number of quanta of surface wave oscillation contained in the system is therefore

$$n=AU/\hbar\omega_r. \tag{12}$$

Since the surface waves are quantized according to the harmonic oscillator, we find for the basic matrix element of excitation from the ground state to the first excited state of the oscillator the expression

$$|H'_k|^2=\frac{\langle H'\rangle^2}{n}=\frac{8\pi Ae^2}{V^2(1+\epsilon)}\frac{\hbar\omega_r k}{[k^2+(\Delta k)^2]^2}. \tag{13}$$

Having now determined the excitation matrix element we can find the scattering coefficient for scattering of the incident electron by polar angle θ and azimuthal angle Ψ into differential solid angle $d\Omega$ by computing the rate at which such scatterings take place. This rate is given on the one hand by multiplying the flux density times the cross sectional area times the chance of scatter in traversing the interface, to, on the other hand, the standard expression from time dependent perturbation theory:

$$A(v/V)\mu(\theta,\Psi)d\Omega=(2\pi/\hbar)d\rho(E)|H'_k|^2. \tag{14}$$

The differential density of states is given by

$$d\rho(E)=\frac{Vp^2}{(2\pi)^3\hbar^3 v}d\Omega, \tag{15}$$

where p, v, and E are the electron momentum, velocity, and energy respectively. Substitution from Eqs. (11, 12, 13 and 15) into Eq. (14) yields for the scattering coefficient

$$\mu(\theta,\Psi)=\frac{e^2}{\pi\hbar v}\frac{2}{1+\epsilon}\frac{\theta_E\theta}{(\theta_E^2+\theta^2)^2}f, \tag{16}$$

where

$$\theta=hk/p, \tag{17}$$

and we have used the abbreviation

$$\theta_E=\hbar\Delta k/p=\hbar\omega_r/(2E). \tag{18}$$

We have included in Eq. (16) a correction factor for the case of non-normally incident electrons, which by straightforward procedures can be shown to be given by the expression

$$f(\theta,\Psi)=\left[\frac{1+(\theta_E/\theta)^2}{\cos^2\alpha}-(\tan\alpha\cos\Psi+\theta_E/\theta)^2\right]^{\frac{1}{2}}, \tag{19}$$

where α is the angle of incidence and Ψ is measured relative to the plane of incidence. It will be noted that for non-normally incident electrons the zero in the scattering pattern no longer coincides with the direction of incidence but is instead shifted to the nonzero scattering angle

$$\theta=\theta_E\tan\alpha,\qquad \Psi=0. \tag{20}$$

Since θ_E is generally a very small angle (less than a milliradian) this shifting of the zero will not generally be observable. Another effect which however should be susceptible to observation is seen by considering Eq. (19) for θ much greater than θ_E:

$$f(\theta,\Psi;\alpha)\approx(1+\tan^2\alpha\sin^2\Psi)^{\frac{1}{2}}. \tag{21}$$

Thus we see that there should be a considerable flaring of the intensity pattern away from the plane of incidence, the more so the greater the angle of incidence becomes. Observation of this feature of the intensity pattern would be further conclusive evidence of the surface wave excitation interpretation of the low-lying characteristic energy losses.

A further quantity of interest is the differential probability for scattering into the conical solid angle $d\Omega=2\pi\theta d\theta$;

$$dP=\mu 2\pi\theta d\theta=\frac{4e^2}{\hbar v(1+\epsilon)}\frac{\theta_E\theta^2 d\theta}{(\theta_E^2+\theta^2)^2}, \tag{22}$$

where for simplicity we will from now on restrict ourselves to the case of normal incidence. Integrating this expression over all scattering angle gives for the total probability of excitation of a surface wave upon passing through an interface the expression

$$P=\pi e^2/\hbar v(1+\epsilon). \tag{23}$$

Upon replacing ϵ by unity (vacuum) this reduces to Ritchie's result, taking into account the factor of two arising from the two surfaces of a metal film in his case compared to the one surface in our case. It should be noted that in interpreting Eq. (23) as expressing the probability for surface wave excitation relative to the probability of finding any given electron emerging without any energy loss, the attenuation in passing through the metal film and dielectric medium is taken into con-

sideration. As a specific example, Eq. (23) gives for aluminum with 10 kilovolt incident electrons about 2.5% excitation probability for each oxidized surface or altogether about 5% intensity of the low-lying characteristic energy loss, in good order of magnitude agreement with the experimental observations.

So far as the authors are aware, no attempts have been made to study the angular dependence of the intensity of the low-lying loss expressed by Eq. (16). Aside from the azimuthal dependence for non-normally incident electrons discussed above, it would be highly desirable to test quantitatively the predicted falloff with scattering angle which is expressed by Eq. (16). A special feature of this angular dependence is that it drops much more rapidly than the intensity of the bulk excitation coefficient as the scattering angle increases. Therefore, if one desires to make experiments which are free from surface effects, it is clear that one need only arrange the experimental measurements so that scatterings by very small angles of less than say two or three milliradians are explicitly masked out and excluded.

Before passing on in the next section to consider the effect of finite oxide thickness we want now to establish upper bounds on two effects which are ignored for the sake of simplicity in the present work. The first effect is that of retardation and the use of the electrostatic potential, rather than the electrodynamic potentials of Maxwell's theory. The size of the percentage error committed on this account can be estimated roughly by considering the ideal case of a semi-incident plasma bounded by vacuum. Then we see from Eq. (22) that the most probable angle of scattering is θ_E, corresponding to a wave number of $k=\Delta k$. The exact dispersion relation taking into account retardation for the plasma surface oscillations has been worked out by Fano[2] and more recently in a different way by one of the authors (E.A.S.). The formula is quoted in reference 10 as Eq. (16) and for the present case of a relatively large wave number, it reduces to a fractional decrease in the resonant frequency of

$$\frac{\Delta\omega}{\omega_p/\sqrt{2}}\approx-\frac{1}{8}\left(\frac{\omega_p}{c\Delta k}\right)^2=-\frac{1}{4}\left(\frac{v}{c}\right)^2, \tag{24}$$

which for 10 kev incident electrons ($\frac{1}{5}$ the velocity of light) is only one percent. It is therefore clear that the retardation corrections become only significant for relativistic incident electrons, and that they may be legitimately neglected for the actual energy loss experiments. The second approximation which we wish to justify is that of neglecting the finite thickness of the metal films and treating them as semi-incident samples, insofar as the surface waves are concerned. Here again for simplicity we restrict ourselves to the case of a metal film bounded by vacuum. For a finite thickness the waves on the two different surfaces interfere with one another and set up two different types of normal modes of vibration, as shown in Figs. 1(a) and 1(b).[11] The fractional splitting of these modes of vibration is given approximately by the expression

$$\frac{\Delta\omega}{\omega_p/\sqrt{2}}\approx e^{-\Delta k\tau}, \tag{25}$$

which follows by expanding Ritchie's[1] Eq. (33). The value of the wave number transfer normal to the film Δk is given by

$$\Delta k^{-1}=\frac{v}{\omega_p/\sqrt{2}}=\frac{1}{\pi\sqrt{2}}\frac{v}{c}\lambda_p, \tag{26}$$

where λ_p is the photon wavelength corresponding to the bulk plasmon photon energy, and amounts to 845 angstroms, for aluminum. Taking again the case of 10-kev incident electrons, we find $(\Delta k)^{-1}=38$ angstroms. For a thickness of $\tau=3\Delta k^{-1}=114$ angstroms, we would obtain a splitting of five percent. Since the films used in the transmission experiments are generally considerably thicker than this, it is clear that the interference of the two surfaces can legitimately be neglected, and that one can use the picture of Fig. 1(c), for a semi-infinite metal sample.

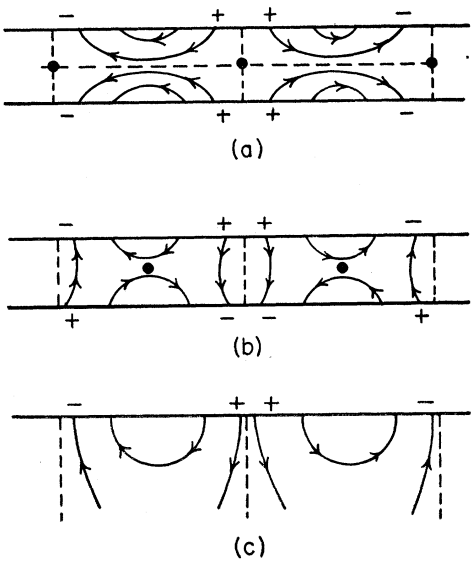

FIG. 1. Plasma oscillations in a metal film. The waves on the two surfaces interfere giving two different normal modes of higher and lower frequency as shown in Figs. 1(a) and 1(b), respectively. For actual characteristic energy loss experiments the wavelengths are sufficiently small, so that the waves to a good approximation can be considered decoupled and the picture of the semi-infinite plasma (c) applies.

III. DIELECTRIC LAYER

In this section we study the waves at the surface of a semi-infinite plasma bounded by a dielectric layer of

[11] This interpretation of the dispersion relation in terms of interference of the two surfaces has been reported at the 1958 Washington Meeting of the American Physical Society: E. A. Stern and R. A. Ferrell, Bull. Am. Phys. Soc. 3, 191 (1958).

finite thickness τ, beyond which there is vacuum. Thus, in the Cartesian coordinate system we take the dielectric vacuum interface at $z=\tau$. Equation (3) still holds inside the plasma but in the oxide layer and in the vacuum it must be replaced by the more complicated expression

$$\varphi(x,z,t)=\varphi_0\times\begin{cases}\cos(kx-\omega t)[(1+\epsilon_p/\epsilon)e^{kz} \\ \quad +(1-\epsilon_p/\epsilon)e^{-kz}], & 0\leq z\leq\tau \\ [(1+\epsilon_p/\epsilon)e^{2k\tau}+(1-\epsilon_p/\epsilon)] \\ \quad \times\cos(kx-\omega t)e^{-kz}, & z\geq\tau.\end{cases} \tag{27}$$

In order to satisfy the condition of continuity of the normal component of the electric displacement vector at the oxide vacuum interface we must have

$$\frac{\epsilon_p}{\epsilon}=-\frac{1-\gamma e^{-2k\tau}}{1+\gamma e^{-2k\tau}}, \tag{28}$$

where

$$\gamma=\frac{\epsilon-1}{\epsilon+1}. \tag{29}$$

Substituting from Eq. (1) into Eq. (28), we find the dispersion relation

$$\omega=\omega_p\left[\frac{\epsilon+\tanh k\tau}{2\epsilon+(1+\epsilon^2)\tanh k\tau}\right]^{\frac{1}{2}}. \tag{30}$$

It will be noted that either in the limits $\epsilon\rightarrow 1$ or $\tau\rightarrow\infty$ Eq. (30) reduces to Eq. (6a) of the previous section. As we allow τ to increase from 0 to infinity we obtain a monotonic relaxation of the frequency of the surface wave. The principal point which we have to settle in this section is, "How thick does the oxide coating have to be in order to have it give the effects of the limiting case of infinite thickness?" This question can be conveniently investigated for thicknesses relatively large compared to the wavelength by making an expansion of Eq. (30):

$$\frac{\Delta\omega}{\omega_r}\approx\frac{\epsilon(\epsilon-1)}{(\epsilon+1)^2}e^{-2k\tau}. \tag{31}$$

Here $\Delta\omega$ is the amount by which the frequency is raised because of the finite thickness above the completely relaxed value ω_r [Eq. (6a)]. As a specific example, consider aluminum at the intensity maximum $k=\Delta k$ and for a thickness $\tau=\Delta k^{-1}=38$ angstroms. Equation (31) then gives a 6% increase or less than $\frac{1}{2}$ an electron volt in the low-lying characteristic energy loss. Thus it is clear that for oxide coatings of this thickness one can consider them to be essentially of infinite thickness. But for thinner coatings it is necessary to study the distribution of intensity versus characteristic energy loss in more detail.

It is a straightforward but tedious problem to show that the right-hand member of Eq. (16) must be corrected by the factor

$$F=\frac{1+2\gamma e^{-k\tau}\cos(\Delta k\tau)+\gamma^2e^{-2k\tau}}{(1+\gamma e^{-2k\tau})(1-\gamma^2e^{-2k\tau})}, \tag{32}$$

for the case of a finite dielectric layer. This factor approaches unity asymptotically as τ approaches infinity, but in the limit $\tau\rightarrow 0$, F becomes $(1+\epsilon)/2$, which serves effectively to replace ϵ in Eq. (16) by unity, corresponding to the disappearance of the dielectric in this limit. This smooth behavior of F makes it clear, and one can easily verify, that the finiteness of the dielectric layer does not alter in any drastic way the intensity distribution calculated for the ideal case of a semi-infinite dielectric medium. For this reason, and from the fact that we will be interested in the short wavelength limit anyway, in which case F can be replaced by unity, we will not make any further use of Eq. (32) in this paper, and will assume Eqs. (16) and (22) valid for dielectric layers of finite thickness. Figure 2 shows by the top solid curve the dispersion of the surface oscillation frequency versus wave number as given by Eq. (30). The intensity distribution along the scattering angle axis indicates that of Eq. (22) and is to be projected upward to the dispersion curve and then to the left to the characteristic energy loss axis, where it will be seen to yield for the intensity vs energy loss curve a broad, smeared-out loss at an intermediate energy and a sharp line at the completely relaxed energy. From now on we will ignore the broad intermediate energy line because of the damping which can be expected from the absorptive properties of the oxide coating. Thus this line will become completely smeared out and unobservable. However, the line at the completely relaxed frequency, which accumulates due to the lack of dependence of the surface wave frequency on k in the high k limit, will be a line that is observed in practice. Analytically we have as a distribution of the probability of scattering as a func-

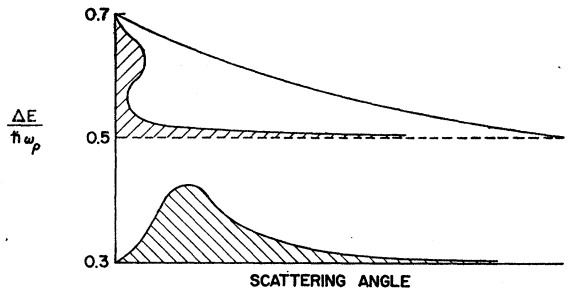

FIG. 2. Energy distribution of intensity. The top solid curve shows the dispersion in the low-lying characteristic energy loss arising from the excitation of surface plasma waves, including the effect of the oxide coating on the metal surface. The lower cross-hatched area shows the distribution of intensity as a function of angle of scattering. Projected up to the dispersion curve and across to the left, the area reappears again as the cross-hatched distribution of intensity vs energy loss. Note the appearance of the line at the completely relaxed value of the characteristic energy loss corresponding to an infinite oxide coating.

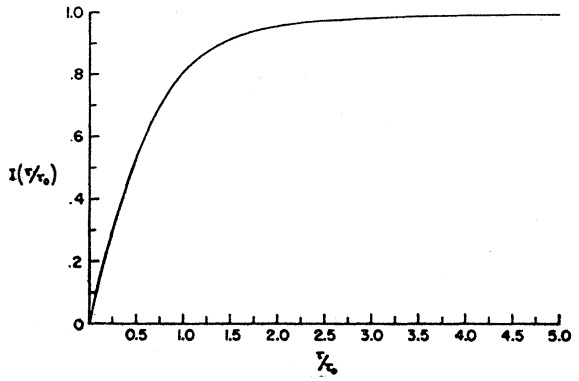

FIG. 3. Relative intensity of low-lying loss versus thickness of the oxide coating. $I(\tau/\tau_0)$ is the ratio of the intensity of the relaxed line for an oxide coating of thickness τ relative to the intensity for an infinite oxide coating. τ_0 is estimated as 41 A for 10-kev electrons on Al. Thus a 20 A coat of Al_2O_3 already gives about one-half of the maximum low-lying intensity.

tion of frequency

$$\frac{dP}{|d\omega|}=\frac{dk}{|d\omega|}\frac{dP}{dk}\propto(\Delta\omega)^{-1}\ln^{-2}\left[\frac{\epsilon(\epsilon-1)\omega_r}{(\epsilon+1)^2\Delta\omega}\right], \quad (33)$$

where the energy shift as before is defined as

$$\Delta\omega=\omega-\omega_r. \quad (34)$$

Thus the intensity distribution per unit energy loss actually becomes infinite at the characteristic energy loss $\hbar\omega_r$. But this infinity will be smeared out and made finite by the instrumental resolution. Therefore, as a measure of the peak intensity which would be actually observed in the experiments, we take the total intensity contained between ω_r and $(1+\beta)\omega_r$, where $\beta^{-1}>$unity is a measure of the resolution of the apparatus. Thus setting

$$\Delta\omega=\beta\omega_r, \quad (35)$$

we find from Eq. (31) that all scatterings contribute to the peak intensity which have wave number greater than

$$k=\frac{1}{2\tau}\ln\frac{\epsilon(\epsilon-1)}{(\epsilon+1)^2\beta}=\frac{\Delta k}{\tau/\tau_0}, \quad (36)$$

where the characteristic thickness is defined by

$$\tau_0=\frac{(\Delta k)^{-1}}{2}\ln\frac{\epsilon(\epsilon-1)}{(\epsilon+1)^2\beta}. \quad (37)$$

For the case of aluminum,[12] 10% resolution ($\beta=0.1$, or 0.7 ev width) and 10-kev electrons, $\tau_0=41$ angstroms.

[12] Note that relaxation increases $(\Delta k)^{-1}$ by about 50%.

Integrating Eq. (22) over all wave numbers greater than the critical wave number gives, relative to the maximum intensity for infinitely thick dielectric layers, the expression

$$I\left(\frac{\tau}{\tau_0}\right)=\frac{4}{\pi}\int_{\tau_0/\tau}^{\infty}\frac{(k/\Delta k)^2 d(k/\Delta k)}{[(k/\Delta k)^2+1]^2}=\frac{2}{\pi}\left[\tan^{-1}\frac{\tau}{\tau_0}+\frac{\tau/\tau_0}{(\tau/\tau_0)^2+1}\right]. \quad (38)$$

This function is plotted in Fig. 3 where it will be seen that the completely relaxed line already obtains about 50 percent of its maximum strength for a thickness of about $\frac{1}{2}\tau_0$ or about 20 angstroms for the case of aluminum oxide on aluminum. Figure 3 illustrates the somewhat surprising result that even for a very thin oxide coating the completely relaxed line appears, but with a low intensity. As the layer thickness is increased, the intensity grows rapidly. Thus the general result of oxidizing a metallic surface is to cause the metal vacuum oscillations to disappear quickly and in their place at a significantly lower frequency to appear the completely relaxed line with rapidly growing intensity. This explains why one does not see a continuous shift from the original line down to the relaxed line, but instead the original line disappears and a new line appears at a separate frequency.

IV. CONCLUSION

The goal of the above work has been to establish that Ritchie's explanation of the low-lying characteristic energy losses is basically adequate to account for all of the observed data, and only needs the natural extension to be taken to account for the oxide coatings on the metallic surfaces. Thus the surface waves give a natural explanation of the low-lying losses without any need of postulating *ad hoc* deviations of the dielectric bulk properties of the metals from relatively ideal behavior. One confirmation of the surface wave theory would be the detection of surface waves existing at the interface of two different plasmas. For example, a double metal film composed of a layer of aluminum in intimate contact with a layer of magnesium should exhibit a new characteristic energy loss at 13 electron volts.

Experimental measurements on the angular dependence of the low-lying losses would be extremely valuable. A measurement of the dispersion of the energy loss as a function of a scattering angle would determine the oxide thickness, while intensity measurements as a function of angle would give a good check on the theory. In particular, it would be very interesting to look for the characteristic flaring of the intensity pattern away from the plane of incidence for non-normally incident electrons.