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Verification of the Anomalous-Skin-Effect Theory for Silver in the Infrared

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The measured infrared reflectance of silver films prepared by rapid evaporation in ultrahigh vacuum was found to be in excellent agreement (0.1%) with values predicted by the anomalous skin effect theory in the wavelength region from 4–24 μ (values of $\omega\tau$ between 15 and 2, where τ is the relaxation time). If a small correction term was included for electron-electron collisions, the agreement could be extended to 1 μ ($\omega\tau\simeq50$). The theoretical curves were determined from values of dc conductivity and Hall constant measured on silver films prepared in the same evaporation as the optical samples. No optical data were used to fit the calculated curves to the experimental data. Silver films of varying degrees of roughness were prepared by evaporating silver onto supersmooth fused-quartz optical flats which had been roughened with calcium fluoride films. It was found that there was no difference between the infrared reflectance of rough and smooth silver samples for roughnesses up to 45 Å rms. Thus $p\simeq1$, a condition usually interpreted as specular reflection of the conduction electrons, for surfaces about an order of magnitude rougher than the value predicted by simple diffraction theory. For rougher surfaces, p dropped rapidly to 0 and, for the roughest surfaces studied (~100 Å rms), the reflectance was somewhat lower than that predicted theoretically.

INTRODUCTION

It is difficult in most cases to unambiguously separate the effects of interband and intraband transitions in metals at high frequencies. In a perfect lattice, however, there is a limiting frequency below which direct interband transitions are forbidden. Indirect interband transitions may occur below this frequency, but if their contribution is negligible and if the limiting frequency is relatively high, as it is for silver, only intraband transitions contribute over a large frequency range. For silver this range covers a large portion of the infrared. Since silver is monovalent and has a nearly spherical Fermi surface, its infrared reflectance should be directly comparable with that predicted by theory. In order to make such a comparison meaningful, however, the experimental requirements for sample preparation are quite stringent. The literature is full of evidence that, if inadequate experimental techniques are used, there is disagreement between theory and experiment. The problem is to determine how closely the theory is followed if optimum sample preparation and measurement techniques are used. Lattice distortion, such as that introduced by mechanical polishing of a bulk material, may strongly affect the reflectance,[1] presumably by both altering the band structure and by breaking down the selection rules. This effect is particularly troublesome in silver which is ductile and thus easily distorted by mechanical polishing. The distorted region is very nearly the same as the 220Å amplitude penetration depth for light in silver.[2] The best method for eliminating lattice distortion at the surface of bulk samples is electropolishing, but this method usually leaves the surface too rough and wavy for precision optical measurements. An undistorted, flat, nearly atomically smooth sample can, however, be prepared by vacuum evaporation. The evaporation should be performed in ultrahigh vacuum to minimize the effect of residual gas. The substrates should be supersmooth and the evaporated silver films should be kept thin, since the theory predicts that surface roughness is a determining factor in the reflection of conduction electrons. This paper reports on optical and electrical measurements made on silver films prepared under the conditions described above, so that they should be suitable for comparison with theory.

Expressions giving the contribution to the reflectance from intraband transitions may be obtained from the classical quasifree electron theory first proposed by Drude and later modified by Zener, Sommerfeld, and others.[3] Maxwell's equations form the basis for the derivation of the Drude theory, but an auxiliary relation, usually the Boltzmann transport equation, must be used to obtain expressions for the frequency-dependent polarizability and conductivity. In the simple theory, which assumes that the field in which the electrons move between collisions is constant, the reflectance is a function of only two material parameters, the dc conductivity σ_0 and the relaxation time τ. The former may be measured directly and the dc value of the latter may be obtained from Hall effect measurements if σ_0 and the effective mass are known.

When the amplitude penetration depth of the incident light becomes comparable to the mean free path of the

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[2] L. E. Samuels and J. V. Sanders, J. Inst. Metals **87**, 129 (1958); L. E. Samuels, in *The Surface Chemistry of Metals and Semiconductors*, edited by H. C. Gatos (John Wiley & Sons, Inc., New York, 1960), pp. 82–106.

[3] F. Seitz, *The Modern Theory of Solids* (McGraw–Hill Book Co., Inc., New York, 1940), pp. 629–642; A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1936), pp. 123–126.

conduction electrons, the simple Drude theory must be modified. This modification, called the anomalous skin effect, was worked out in the late forties and fifties by Reuter and Sondheimer,[4] Dingle,[5] Pippard,[6] and others.[7,8] A surface parameter p is introduced which is related to the probability that the conduction electrons are specularly reflected upon striking the surface. Since these electrons have a de Broglie wavelength which is related to the Fermi energy of the material, one may, by assuming the system is nondegenerate (a poor assumption for metals), calculate approximately how smooth the surface should be before appreciable specular electronic reflection can occur. In general, however, p has been treated as an adjustable parameter and its value has been chosen to give the best fit to the experimental results. The bulk of the published data, mostly based on electrical measurements, indicates that $p\simeq 0$ (usually interpreted as diffuse electronic scattering) not only for metals,[9,10] but even for semiconductors[11] where one would expect specular electronic reflection to occur.[12] On the other hand, it has been reported that $p\simeq 1$ (usually interpreted as specular electronic reflection) not only for the semimetal bismuth,[13] but also for tin, lead,[14] and the noble metals gold[15–17] and silver[17,18] where the electronic wavelength is so short that the surface would seem to have to be nearly atomically smooth for specular electronic reflection to occur.[19] This apparent paradox has been partially resolved by Greene,[20] who points out that $p\simeq 1$ does not necessarily imply that the electronic reflection is specular even in a nondegenerate system, and that, in addition, the conduction electrons in a metal are highly degenerate. The roughness at which p goes from 1 to 0 for a metal may therefore be considerably different from that calculated from simple diffraction theory. No experiments have been previously reported for which surfaces with $p\simeq 1$ have been roughened to the point where $p\simeq 0$.

The theory described above is semiclassical, but quantum mechanical derivations have also been given.[8,21,22] These place the theory on firmer ground but, at temperatures much larger than the Debye temperature, yield expressions of the same form as those derived classically. An exception is the incomplete theory of Van Gelder[22] which introduces the boundary conditions in such a way that additional absorption may occur with a corresponding drop in reflectance. At cryogenic temperatures the photon–multiple-phonon process proposed by Holstein[23] also causes the absorption to be larger than that computed semiclassically. Gurzhi[21] has included this result in his quantum transport equation, and experimental work[24] is in good agreement with his results. The effect is negligible, however, for silver at room temperature.

In the near infrared the measured reflectance of silver drops below that predicted by the anomalous skin effect theory. This reflectance decrease has been attributed to a decrease in the relaxation time τ, which is now no longer given by the Lorentz-Sommerfeld relation. At the plasma frequency for silver, τ is smaller than its dc value by about a factor of 2.[25] The limiting frequency at which τ starts to decrease, which in an ideal crystal is presumably related to electron-electron and electron-lattice interactions, is hard to determine experimentally. The principal difficulty is that poor sample preparation, in addition to contributing impurities, may produce lattice distortion, surface films, or surface roughness, any one of which may cause the reflectance to drop too rapidly with increasing frequency and hence make τ appear to decrease. It is therefore of interest to determine how large the frequency ω can become for carefully prepared samples before the relaxation time begins to show appreciable frequency dependence.

In this paper we will show that if a silver surface is very smooth, the simple Drude theory (which from an experimental point of view is equivalent to the anomalous skin effect modification with $p=1$) is in excellent

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agreement ($\sim$0.1%) with experiment in the infrared for $\omega\tau<15$, or, if a small electron-electron correction is added, for $\omega\tau<50$. The parameters σ_0 and τ used in the calculations were obtained from electrical measurements on films prepared simultaneously with those used for the optical measurements. No optical parameters were used to fit the theory to the experimental reflectance values. We have found that $p\simeq1$ for the reflectance measurements unless the surfaces have an rms roughness of over 45 Å. For roughnesses over 65 Å, $p\simeq0$. The roughness value at which p goes from 1 to 0, although not large, is about an order of magnitude larger than one would naïvely expect from simple diffraction theory and thus provides experimental support for Greene's[20] conclusion that $p\simeq1$ for a metal does not necessarily imply that the metal-air interface is smooth compared to the de Broglie wavelength.

DRUDE THEORY

Maxwell's equations form the basis for the derivation of the Drude theory. From the Gaussian form of the wave equation, we have the relation

$$\nabla^2\mathbf{E}+\frac{\omega^2}{c^2}\mathbf{E}-j\frac{4\pi\omega}{c^2}\mathbf{J}=0, \tag{1}$$

where $\mathbf{J}=(j\omega\alpha+\sigma)\mathbf{E}$ is the current density, $\mathbf{E}$ is the electric field having circular frequency ω, and c is the velocity of light. The polarizability α and conductivity σ are both frequency-dependent. They may be written as the sum of contributions from various mechanisms:

$$\alpha=\alpha_{\text{intraband}}+\alpha_{\text{interband}}+\alpha_{\text{lattice absorption}}+\alpha_{\text{localized states}}+\alpha_{\text{core potential}}+\cdots, \tag{2}$$

$$\sigma=\sigma_{\text{intraband}}+\sigma_{\text{interband}}+\sigma_{\text{lattice absorption}}+\sigma_{\text{localized states}}+\cdots. \tag{3}$$

Since σ is the real part of the complex conductivity and hence is related to the energy absorbed by a material, the various components of σ are nonzero only in frequency intervals where absorption from the particular mechanism occurs. However, the components of α may be nonzero even in frequency intervals other than those where absorption from those mechanisms takes place, and a complete theory must take this effect into account.

The values of the various components of α and σ cannot be evaluated from electromagnetic theory. Auxiliary relations are necessary, and their correct forms are a primary objective of solid-state physics. Both quantum mechanical and classical treatments employing Boltzmann's transport equation have been used to determine $\alpha_{\text{intraband}}$ and $\sigma_{\text{intraband}}$. Briefly, the classical argument is as follows[4]: If f is the velocity distribution function for conduction electrons in a metal, and t is time, under steady-state conditions $df/dt=0$. Letting $f=f_0+f_1$, where f_0 is the Fermi-Dirac distribution function and f_1 is a small perturbation caused by an electromagnetic field, the condition

$$df/dt=(df/dt)_{\text{field}}-(df/dt)_{\text{collisions}}=0 \tag{4}$$

yields the Boltzmann equation

$$\frac{\partial f_1}{\partial t}+\mathbf{v}\cdot\nabla_r f+\mathbf{a}\cdot\nabla_v f=-f_1/\tau, \tag{5}$$

where $\mathbf{r}$, $\mathbf{v}$, and $\mathbf{a}$ are the electronic position, velocity, and acceleration, respectively, and

$$\mathbf{a}=-(e/m^*)[\mathbf{E}+(\mathbf{v}/c)\times\mathbf{H}],$$

where $\mathbf{H}$ is the magnetic-field strength. If the field is removed, f_1 decays as $e^{-t/\tau}$ where τ is the relaxation time, i.e., time required for f to return approximately to its unperturbed state. If it is assumed that upon collision an electron loses memory of its previous momentum, τ may be loosely interpreted as the mean time between electronic collisions. The perturbation f_1 will have the frequency ω of the exciting field, and at high frequencies where $\omega\tau>1$ the relaxation time may become frequency-dependent. This dependence, which may result from electron-electron interactions or other causes,[26,27] is not predicted by the semiclassical theory.

When terms involving the magnetic field and the product $\mathbf{E}\cdot\nabla_v f_1$ are neglected we have, from (5), the fundamental equation

$$\frac{\partial f_1}{\partial z}+f_1\frac{(1+j\omega\tau)}{v_z\tau}=\frac{e}{m^*v_z}E_x\frac{\partial f_0}{\partial v_x}. \tag{6}$$

If the penetration depth of the field is large enough that the contribution of $\partial f_1/\partial z$ can be neglected, f_1 can be solved for directly. Then $(J_x)_{\text{intraband}}$, the current density in the x direction resulting from the conduction electrons, is

$$(J_x)_{\text{intraband}}=-Ne\int_{-\infty}^{\infty}f(v_x)v_x dv_x=\frac{\sigma_0E_x}{1+j\omega\tau}, \tag{7}$$

where N is the number of conduction electrons per unit volume and σ_0 is the dc conductivity. Since Eq. (7) gives the relation between $\mathbf{J}$ and $\mathbf{E}$ for intraband transitions, the expressions for $\alpha_{\text{intraband}}$ and $\sigma_{\text{intraband}}$ may now be obtained from the definition of $\mathbf{J}$ following Eq. (1). In terms of $\bar{n}=n-jk$, the complex index of refraction, they are

$$n^2-k^2=1-4\pi\alpha_{\text{intraband}}+4\pi\alpha_0=1-\frac{4\pi\sigma_0}{\tau(\omega^2+\tau^{-2})}+4\pi\alpha_0, \tag{8}$$

$$nk=\frac{2\pi\sigma_{\text{intraband}}}{\omega}=\frac{2\pi\sigma_0}{\omega\tau^2(\omega^2+\tau^{-2})}. \tag{9}$$

Note that although we have assumed that all of the

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[26] C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1044 (1964).

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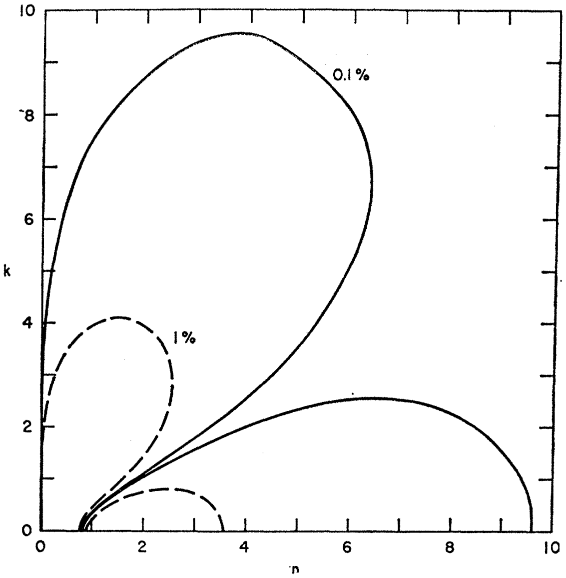

FIG. 1. Range of validity of Eq. (11). The calculated value of R is in error by less than 0.001 *outside* the solid lines, and by less than 0.01 *outside* the dashed lines.

absorption in the frequency range considered arises from intraband transitions, we have added the term α_0 to account for the contribution to α made by other absorption mechanisms operating in other frequency ranges. Equations (8) and (9) are the basic equations of the Drude theory. The normal incidence reflectance of a metal may now be calculated from material parameters since

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}, \tag{10}$$

and the values of n and k are given in Eqs. (8) and (9).

In certain wavelength regions, R may be expressed explicitly in terms of σ_0, τ, and α_0. If $n>1$ and $k>1$, the reflectance of a metal at normal incidence is approximately[17]

$$R=\exp[-4n/(n^2+k^2)]. \tag{11}$$

Figure 1 shows the range of values of n and k for which Eq. (11) is valid. The reflectance is in error by less than 0.1% for values of n and k which fall outside the solid line. Since $n\gg1$ and $k\gg1$ for metals in the infrared, Eq. (11) is an excellent approximation in this region. A general expression for the infrared reflectance of a good conductor is then obtained by substituting (8) and (9) into (11)[28]:

$$R=\exp\{-(2\omega/\pi\sigma_0)^{1/2}[(\omega^2\tau^2+1)^{1/2}-\omega\tau]^{1/2}\times[1+g(\alpha_0)]\}, \tag{12}$$

where

$$g(\alpha_0)=\alpha_0[\omega(\omega^2\tau^2+1)^{1/2}+2\omega^2\tau]/2\sigma_0\,. \tag{13}$$

Equation (13) is the first-order term in an expansion in powers of $4\pi\alpha_0$. However, the error in R made by using Eq. (13) in place of the whole expansion is less than 0.001 for values of $4\pi\alpha_0<10$. For silver $4\pi\alpha_0\simeq2$, as can be determined from a Kramers-Kronig evaluation near the absorption edge for interband transitions.[25] At a wavelength of 1 μ ($\omega\tau\simeq70$, where $\tau\simeq3\times10^{-14}$ sec), $g(\alpha_0)=0.057$, making a difference in R of only 0.0002. At longer wavelengths $g(\alpha_0)$ is still smaller and is thus negligible for silver in the infrared.

If $\omega\tau\ll1$, Eq. (12) reduces to the Hagen-Rubens relation

$$R=1-(2\omega/\pi\sigma_0)^{1/2}, \tag{14}$$

and the reflectance is determined only by the dc conductivity. For good conductors this relation is valid only in the far-infrared and microwave regions.[29] At higher frequencies where $\omega\tau\simeq1$, both τ and σ_0 must be known. As long as τ retains its dc value, it may be calculated from the Lorentz-Sommerfeld relation

$$\tau=m^*\sigma_0/Ne^2, \tag{15}$$

where m^* may be determined from specific heat data[30] or from band calculations, and for silver is very nearly equal to m, the free-electron mass; σ_0 may be determined from the measured conductivity; and N may be determined from a Hall-effect measurement. For silver, N should also be calculable to a good approximation from the valence, one free electron per atom. The reflectance is thus calculable entirely from nonoptical parameters in wavelength regions where the Drude theory holds and τ is given by Eq. (15).

ANOMALOUS SKIN EFFECT

The above analysis is based on the assumption that the first term in Eq. (6) is negligible. This assumption is valid only when

$$\delta/l\gg2/(1+\omega^2\tau^2), \tag{16}$$

where $l=\tau v_F$ is the mean free path of the conduction electrons (v_F is the Fermi velocity) and

$$\delta=1/\mathrm{Re}\left[\frac{(2\pi\sigma_0\omega)^{1/2}(1+j)}{c(1+j\omega\tau)^{1/2}}\right]=\frac{\lambda}{2\pi k} \tag{17}$$

is the amplitude penetration depth[31] of the light. At low frequencies where $\omega\tau\ll1$, Eq. (16) requires that δ be much greater than $2l$. Since l is a constant in this region,

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[28] If $\omega\tau\gg1$, Eq. (12) reduces to $R=1-(\pi\sigma_0\tau)^{-1/2}$. The reflectance is then wavelength-independent at high frequencies so long as Eq. (11) holds.

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[31] The amplitude penetration depth is sometimes taken to be the low frequency skin depth $\delta_0=c/(2\pi\omega\sigma_0)^{1/2}$. Although this approximation is valid at microwave frequencies, it is only approximately correct at optical frequencies. For example, for silver at a wavelength of 2 μ it is in error by about a factor of 4. The approximation given by Gurzhi *et al.* (Ref. 39) which is obtained by expanding Eq. (17) to give $\delta\sim\delta_0[1+(\omega\tau)^{-2}]^{1/4}$, is not appreciably better, since the factor of multiplying δ_0 is 1.0002 for silver at 2 μ.

and since, from Eq. (17), δ is proportional to $1/\omega^{1/2}$, we see that Eq. (16) is satisfied for sufficiently low frequencies regardless of the value of τ or σ_0. At high frequencies where $\omega\tau \gg 1$, the requirement is that $\delta/l \gg 2/\omega^2\tau^2$ in order for the Drude theory to hold. In this region, since δ is independent of frequency and l is constant, at sufficiently high frequencies the inequality will again hold regardless of the value of τ or σ_0. At intermediate frequencies Eq. (16) may not be satisfied even at room temperature, so that none of the terms in Eq. (6) can be neglected. In this so-called anomalous skin effect region a correction must be applied to the value of the reflectance calculated from Eqs. (8)–(10) or from Eq. (12). This correction is a function of a surface parameter p which is related to the probability that a conduction electron will be reflected specularly at the surface of a material. It has been taken to be an experimental parameter, and in most investigations, the best fit has been obtained by letting $p \simeq 0$.

Figure 2 shows the theoretical reflectance of silver calculated from the simple Drude theory (short dashed curve) along with the corrections in the anomalous skin effect region assuming $p=1$ (solid curve) and $p=0$ (long dashes). These curves cannot be directly compared with experiment at wavelengths shorter than about 1 μ since absorption resulting from interband transitions and other factors has not been included, τ has been assumed to be constant, and α_0 has been set equal to 0. However, in the infrared and at longer wavelengths, the curves should be directly comparable with experimental values. The curve showing the Drude theory reflectance was calculated from Eqs. (8)–(10) and (15) assuming σ_0 to be the dc conductivity of bulk silver. The value of N in Eq. (15) was calculated by assuming one free electron per atom, and $m^*=m$. No adjustable parameters were included in the calculations. The $p=1$ curve was obtained from the integrals given by Reuter and Sondheimer.[4] Since the graphical results in their Fig. 2 were primarily for low temperatures, it was necessary to program their Eqs. (55) and (57) for a computer and calculate values for room temperature. The results for three values of their parameter α are shown in Fig. 3. These correspond to room temperature conditions for silver, gold, and aluminum. The curves give the log of the ratio of the absorption $(1-R)$ calculated from the anomalous skin effect theory for $p=1$ to that given by the Drude theory. Note that this ratio reaches a maximum for silver for $\omega\tau=2.3$, corresponding to a wavelength of 30 μ. The maximum of this ratio thus corresponds to the minimum in the solid curve in Fig. 2, where the reflectance is about 0.0008 lower than the Drude theory curve. The $p=0$ curve in Fig. 2 was obtained from numbers given by Dingle[5] in his Table III. Again, no adjustable parameters were used. This curve lies about 0.0035 below the other two curves for wavelengths between 3 and 0.3 μ $(23<\omega\tau<230)$ and gradually approaches the other curves at longer wavelengths. The difference in reflectance between the $p=1$ and $p=0$ curves is measurable experimentally with a good reflectometer, and, as will be discussed in the "Experimental" section, we have observed reflectances corresponding to both these values of p.

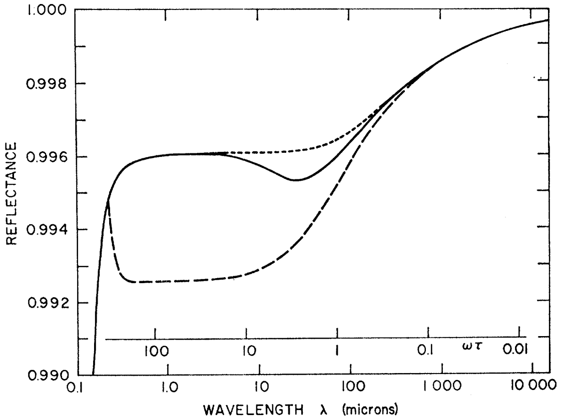

FIG. 2. Reflectance of silver calculated from the anomalous skin effect modification of the Drude theory assuming bulk dc conductivity and 1 free electron per atom. The solid curve is for $p=1$, and the long dashed curve for $p=0$. The simple Drude theory is given by the short dashed curve and connecting solid curve. Since absorption caused by interband transitions and other effects has not been included, these curves cannot be directly compared with measured values for wavelengths shorter than about 1 μ.

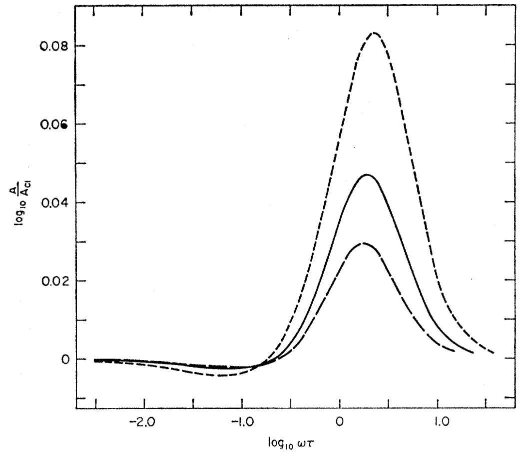

FIG. 3. Ratio of absorption $(1-R)$ calculated from the anomalous skin effect theory for $p=1$ to that given by Drude theory (see Ref. 4, Fig. 2). Values of $\alpha/\omega\tau$ are 4.244 for the short dashed curve, 1.850 for the solid curve, and 0.995 for the long dashed curve, corresponding to room temperature conditions for silver, gold, and aluminum, respectively.

Thus, far the discussion has not indicated how rough a surface must be before $p \simeq 0$. One might at first suppose that $p=1-W_s$ where W_s is the probability, calculated from diffraction theory, that the electron would be diffusely scattered. A value for $1-W_s$, and hence for W_s, may be obtained from the de Broglie wavelength λ_D. For a quasifree-electron gas the Fermi energy E_F is given by

$$E_F=(\pi^2\hbar^2/2m^*)(3N/\pi)^{2/3}=P^2/2m^*, \tag{18}$$

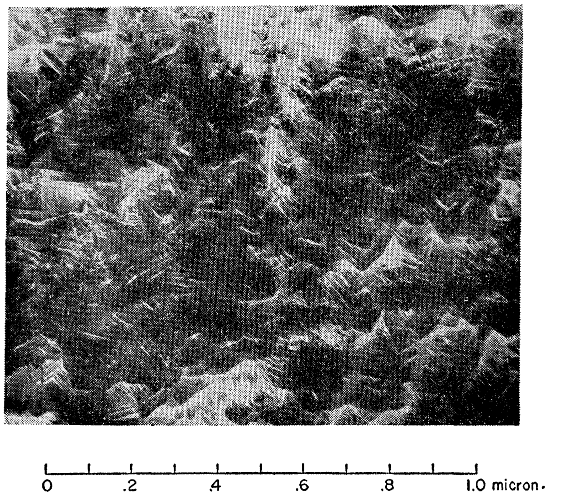

FIG. 4. Electron micrograph of a calcium fluoride film. Note that detail of the order of 0.01 μ (100 Å) can be seen.

where $P=h/\lambda_D$ is the crystal momentum. Therefore

$$\lambda_D=2(\pi/3N)^{1/3}. \quad (19)$$

For a cubic lattice there are ν/a^3 lattice points per unit volume where a is the lattice constant, and ν the number of lattice points per unit cell. A body-centered-cubic lattice has $\nu=2$, while in a face-centered-cubic lattice $\nu=4$. If η is the number of conduction electrons per atom, we have

$$N=\eta\nu/a^3. \quad (20)$$

Solving for λ_D for silver by substituting Eq. (20) into Eq. (19) and taking $\nu=4$, $a=4.08$ Å, and $\eta=1$, gives silver conduction electrons a de Broglie wavelength of 5.22 Å.

We now can estimate W_s. Consider that we have an electron with a wavelength λ_D incident on a (fictitious) continuous surface whose rms roughness is ρ. If the surface has a Gaussian height distribution, the specular reflectance at an angle of incidence θ is[32]

$$\exp[-(4\pi\rho\cos\theta/\lambda_D)^2]. \quad (21)$$

If the incoming electrons are incident equally from all angles, the probability of specular reflection, $1-W_s$, is then given by

$$1-W_s=\frac{1}{2\pi}\int_0^{2\pi}d\phi\int_0^{\pi/2}\sin\theta\cos\theta \times\exp[-(4\pi\rho\cos\theta/\lambda_D)^2]d\theta =(\lambda_D/4\pi\rho)^2\{1-\exp[-(4\pi\rho/\lambda_D)^2]\}. \quad (22)$$

Letting $1-W_s=0.01$ be the criterion for negligible specular reflection, from Eq. (22) $\rho\simeq0.8\lambda_D$, or 4.2 Å rms. Thus the surface must be nearly atomically smooth for specular electronic reflection to occur in a nondegenerate system. One may argue that diffraction from lattice points at the surface should be considered rather than approximating the surface by a continuous interface. Müser[19] has carried out an approximate analysis of this type and has reached about the same conclusions as those obtained above.

Greene[20] has performed a careful analysis of the validity of the boundary condition defining p, which may be written

$$f_1(v_z)=pf_1(-v_z) \text{ at } z=0+ \text{ with } 0\leq p\leq 1. \quad (23)$$

He concludes that Eq. (23), which gives a relationship between the velocity of the incident and reflected conduction electrons, is valid for metals provided that there is no magnetic field, the energy bands are flat, and surface scattering does not affect the bulk scattering of the incident electrons. However, p is equal to the probability W_0 that an electron will be specularly reflected by a rough surface only if the scattering is isotropic. For anisotropic scattering there is a weighting factor which acts to make electrons scattered at small angles to the specular direction contribute to p almost as if they were specularly reflected. In addition W_0, which Greene calls the kinetic specularity, equals $1-W_s$ only if the system is nondegenerate. For a degenerate system, such as the electron gas in a metal at normal temperatures, one has an additional weighting factor arising from the Pauli exclusion principle, which is present because not all states into which an electron could be scattered are unoccupied. Thus p is in general larger than W_0 and may be nearly unity even when $1-W_s$ approaches 0. For this reason, p can be $\simeq1$ for values of ρ much larger than 4.2 Å rms. How much larger is one of our objects to determine.

EXPERIMENTAL

The silver films used for the measurements were prepared by evaporation in ultrahigh vacuum. The silver, of 99.999% purity, was deposited at approximately 25 Å/sec from a tungsten source. Although the pressure in the vacuum chamber initially rose into the 10^{-8}-Torr range when the silver was being melted, during evaporation the pressure remained in the 10^{-9}-Torr range. Film thicknesses, which were monitored during evaporation with an oscillating quartz monitor and later measured interferometrically, were in the 650–1000 Å range. These films were thick enough to be opaque in the infrared but thin enough to contour the surface on which they were deposited without adding appreciable roughness because of the silver crystallites. The smooth surfaces onto which the silver films were evaporated were 1.5-in. fused quartz optical flats specially polished to a supersmooth finish.[33] The measured roughness of

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[32] H. Davies, Proc. Inst. Elec. Engrs. (London) **101**, 209 (1954); H. Hasunuma and J. Nara, J. Phys. Soc. Japan **11**, 69 (1956); H. E. Bennett and J. O. Porteus, J. Opt. Soc. Am. **51**, 123 (1961); H. E. Bennett, *ibid.* **53**, 1389 (1963).

[33] R. W. Dietz and J. M. Bennett, Appl. Opt. **5**, 881 (1966).

these surfaces, coated with either silver or aluminum, was about 7 Å rms. Two methods were used to measure surface roughness, a reflectance method[34] and an interferometric method,[35] and good agreement was obtained between them. The sensitivity of either method to differences in height is at least an order of magnitude better than that obtainable with an electron microscope.

Since it was desired to have surfaces which were rough on an atomic scale, coarsely polished glass or metal surfaces were not satisfactory. These surfaces can be made with surface roughnesses of the desired magnitudes, but the lateral dimensions of the irregularities are of the order of fractions of a millimeter rather than tens of angstroms. Such surfaces do not show the decrease in reflectance found for the atomically rough surfaces. Atomically rough surfaces were produced by depositing calcium fluoride on supersmooth substrates prior to the silver deposition. By varying the thickness of the calcium fluoride and by baking it before the sliver deposition, various roughnesses could be achieved. In order to produce the roughest surfaces, a second layer of calcium fluoride was added followed by a second baking. Under the evaporation conditions described, calcium fluoride forms microcrystallites such as those shown in the electron micrograph in Fig. 4. From this micrograph it is clear that the lateral dimensions of the smooth crystallite faces are less than 1000 Å, and detail of the order of 100 Å can be observed. The height variations, determined from specular reflectance measurements, are of comparable magnitude so that the resulting surface is rough on an atomic scale.

The roughness of the silver-coated calcium fluoride surfaces was obtained by measuring the reflectance R of the rough surface relative to that R_0 of a very smooth surface of the same material. If the distribution of surface irregularities is Gaussian, the relative reflectance at normal incidence is[32]

$$R/R_0 = \exp[-(4\pi\rho/\lambda)]^2, \tag{24}$$

where ρ is the rms roughness and λ the wavelength. Although R/R_0 for the rough calcium fluoride surfaces did not fit a Gaussian height distribution function for all values of R/R_0, it approximated the Gaussian function for $R/R_0 > 0.90$.

In order to guard against possible differences in the silver on the rough and smooth surfaces, both substrates were coated in the same evaporation. The relative reflectance of the rough surfaces and the absolute reflectance of the smooth silver surfaces were measured using the absolute reflectometer described previously.[35,36] This instrument is capable of measuring absolute or relative reflectance with an accuracy of ±0.001 and a precision of better than ±0.0004. Details of the analysis of the data, including how the variation of the infrared reflectance with surface roughness in the anomalous skin effect region was determined, will be described in the "Results" section.

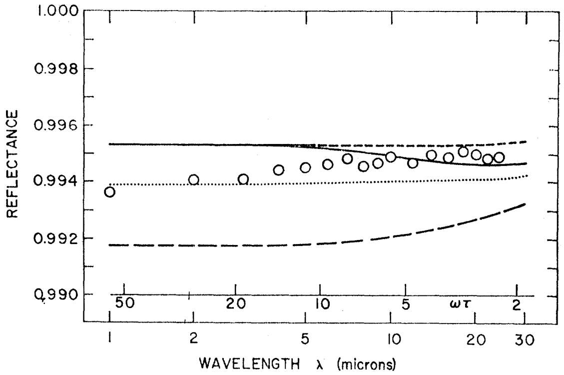

Fig. 5. Calculated and measured infrared reflectance of silver. The circles are experimental points averaged for several films. Calculated values for a conductivity of 87% of bulk are: solid curve, $p=1$; long dashed curve, $p=0$; and short dashed curve, simple Drude theory. The dotted curve was calculated from the simple Drude theory using a conductivity of 67% of bulk. Note that these curves are lower than those in Fig. 2 because of the different conductivity values used.

The electrical measurements, dc conductivity and Hall coefficient, were made on another silver-coated supersmooth quartz sample prepared in the same evaporation. A photoetched mask was used to give the samples a reproducible and measurable shape. The dc conductivity could be determined with an uncertainty of about 2%, the limiting factors being the differences between films and the uncertainty in the film thickness. Film thickness was measured interferometrically using fringes of equal chromatic order,[35,37] and was good to about ±6 Å, the residual error being caused largely by film nonuniformities. The Hall coefficient, which was measured using a six-contact dc method with field and current reversal,[38] could be determined with an uncertainty of about 2.5%. Particular care was taken to reduce the Ettingshausen voltage to a negligible value.

RESULTS

Figure 5 shows the measured reflectance of silver films deposited in ultrahigh vacuum on supersmooth substrates. The reflectance was quite reproducible, and the circles represent average values for several films. The solid and long dashed lines are the theoretical reflectance curves calculated for $p=1$ and $p=0$, respectively, while the short dashed line is the reflectance calculated from the simple Drude theory. The parameters used in the calculations were the measured dc conductivity $\sigma_0 = 4.85 \times 10^{17}$ sec^{-1}, and the Hall constant yielding a value of 1.09 conduction electrons/atom and

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[34] H. E. Bennett, J. Opt. Soc. Am. 56, A1423 (1966).

[35] H. E. Bennett and J. M. Bennett, in *Physics of Thin Films*, edited by G. Hass and R. E. Thun (Academic Press, Inc., New York, 1967), Vol. IV, pp. 1–96.

[36] H. E. Bennett and W. F. Koehler, J. Opt. Soc. Am. 50, 1, (1960).

[37] J. M. Bennett, J. Opt. Soc. Am. 54, 612 (1964).

[38] O. Lindberg, Proc. IRE 40, 1414 (1952).

$\tau = 2.99\times10^{-14}$ sec. More will be said about the electrical measurements later. The excellent agreement between the experimental points and the $p=1$ curve (less than 0.001 difference for $\omega\tau<15$) is significant since the theoretical curves were not fit to the optical data. The $p=0$ curve is outside the probable error of the experimental points and leads one to conclude that $p\simeq1$ for our silver films. This result does not necessarily contradict the large body of published data for which the best fit could only be obtained by letting $p\simeq0$. The surfaces used in our experiments were very smooth and had a measured roughness of about 7 Å rms, considerably less than the 20–40 Å rms roughness of commercial optical flats.[33] Many of the experiments reported in the literature were performed on samples which may well have been even rougher than good commercially available optical flats. It is difficult to judge how rough they were, however, since the surface roughness is always unreported.

The experimental values of the reflectance increase with increasing wavelength, so that the shape of the measured curve most nearly approximates that of the simple Drude theory. We have never observed a decrease in reflectance with increasing wavelength for any silver films, as predicted by the anomalous skin effect modification with $p=1$. The difference between the $p=1$ curve and the simple Drude theory is rather small, however, only 0.0008 at most, and could easily be accounted for if a small amount of additional absorption occurred at the shorter wavelengths. Such absorption might result from indirect interband transitions, impurity scattering, etc. A small decrease of this type presumably results from electron-electron scattering. Gurzhi[27,39] has derived an approximate relation for the electron-electron collision frequency ν_{ee} which is valid if $\hbar\omega\ll E_F$ and $kT\ll E_F$:

$$\nu_{ee}=\omega_0(kT/\hbar\omega_0)^2[1+(\hbar\omega/2\pi kT)^2], \tag{25}$$

where k is the Boltzmann constant, T the absolute temperature, and ω_0 the plasma frequency. If ν_{el} is the electron-phonon collision frequency, Eq. (15) gives $1/\nu_{el}$ which we have assumed is equal to τ. However, if both electron-phonon and electron-electron collisions are included, $\tau=1/(\nu_{el}+\nu_{ee})$, and τ is a constant only as long as the contribution made by ν_{ee} is negligible. The decrease in the infrared reflectance of silver caused by ν_{ee} is very small, amounting to only 0.0005 at a wavelength of 1 μ, and becomes much smaller at longer wavelengths. However, if it is included, it makes the calculated and measured reflectance values agree within 0.001 for values of $\omega\tau<50$.[40] This fit is quite remarkable since τ might be expected to become wavelength-dependent for values of $\omega\tau>1$.

Van Gelder's modification of the quantum-mechanical treatment of the anomalous skin effect[22] predicts additional absorption in the infrared region where $\omega\tau>1$. Although it is difficult to determine the exact magnitude of this additional absorption for silver, he suggests that the decrease in reflectance should be about the same as that ascribed to surface roughness in the classical theory, i.e., about 0.003 for silver. If so, it is clear that this modification destroys the good agreement found between theory and experiment.

Much of the preceding discussion depends on the values of σ_0 and τ used in the calculation of the $p=1$ and $p=0$ curves in Fig. 5. Several silver films, having thicknesses from 650–1000 Å, were used for the electrical measurements. The Hall constant for these films was independent of film thickness and gave 1.09 conduction electrons/atom, in good agreement with the value of 1 electron/atom predicted from the valence of silver. The average dc conductivity was about 67% of the bulk value. Thicker films had the same infrared reflectance but showed a higher conductivity; one such film about 3000 Å thick had a conductivity of 87% of the bulk value. The variation of resistivity (or conductivity) with film thickness was similar to that obtained by Reynolds and Stilwell,[10] whose paper is often quoted as evidence that $p\simeq0$ for evaporated metal films, since the resitivity varies with film thickness. An alternate explanation is that the change in resistivity with thickness arises in large part from agglomeration in the film. Chopra *et al.*[16] have pointed out that, in the case of evaporated gold films on heated glass substrates, the experimental resistivities can be matched theoretically by assuming that the initial island structure connected by thin bridges consists of metal having bulk resistivity. If the islands and bridges grow at the same rate, the film resistivity, calculated on the assumption of a uniform film thickness, decreases hyperbolically, in good agreement with experiment. A second possible explanation is that the initial layers of the metal near the metal-substrate interface are disordered and hence have a higher resistivity than layers farther from the interface. In either case, since the reflectance measurements sample only the upper layers of the film, while the resistance measurements average its entire cross section, one would expect the measured reflectance of fairly thin films to be higher than that calculated from the measured resistance. This is indeed the case. In Fig. 5 the dotted curve is calculated using a value of σ_0 determined from the average measured dc conductivity of the 650–1000 Å films (67% of the bulk value). The simple Drude theory was used for the calculation; with the anomalous skin effect correction for $p=1$, the long-

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[39] R. N. Gurzhi, M. Y. Azbel', and H. P. Lin, Fiz. Tverd. Tela **5**, 759 (1963) [English transl.: Soviet Phys.—Solid State **5**, 554 (1963)].

[40] For values of $\omega\tau>50$, the measured reflectance of silver drops rapidly. The decrease in reflectance near the band edge for interband transitions is too large to be accounted for by α_0 in Eq. (8), and suggests that τ is frequency dependent in this region. Additional evidence is that the experimental value of τ at the plasma frequency is about 1.6×10^{-14} sec, over a factor of 2 lower than the value calculated from the bulk conductivity and 1 conduction electron/atom.

wavelength reflectance would have dropped the same way the solid curve dropped from the short dashed curve, making the long-wavelength agreement even worse. Since the measured infrared reflectance was independent of film thickness but the resistivity continued to decrease with increasing film thickness, it seemed reasonable to choose a value of resistivity which was as nearly a bulk value as possible for the evaporated silver films. The work of Chopra *et al.* on gold[16] showed that the resistivity of films thicker than about 1000 Å reached a constant value which was different from bulk, and furthermore which depended on the substrate and type of film preparation used. Thus, we chose for our "bulk-film" value the measured σ_0 of 87% of bulk for the thickest film measured and used this value to compute the solid and dashed curves in Fig. 5. We feel this choice of conductivity is reasonable since the effect of the film-substrate interface should be considerably less than with thinner films.

Thus far we have described only reflectance measurements of silver films deposited on very smooth substrates. We have also found that by increasing the roughness of the substrates (by depositing varying amounts of calcium fluoride on smooth quartz substrates) it is possible to decrease the reflectance of silver in the infrared. The magnitude of the reflectance decrease is in approximate agreement with that predicted for going from $p=1$ to $p=0$. There is another effect, however, which must be separated from the specular and diffuse electronic scattering. Rough surfaces also scatter light, so that if a small acceptance angle reflectometer is used, the measured reflectance values decrease in a manner predicted by Eq. (24). Note that this optical scattering is very wavelength-dependent, so that if ρ is less than 100 Å, the major portion of the scattering occurs in the near infrared, visible, and at shorter wavelengths. Even for films as rough as 100 Å, the decrease in reflectance caused by optical scattering is less than 0.001 for wavelengths longer than 4 μ. On the other hand, the decrease in reflectance caused by diffuse electronic scattering within the film varies much more slowly with wavelength. It is possible to separate the two effects by obtaining a value of ρ from relative reflectance measurements in the visible, calculating the decrease in reflectance caused by optical scattering for the near infrared wavelengths, and then applying this correction to the measured points. This process is illustrated in Fig. 6 where the circles and squares are 1 minus the measured relative reflectance values $(1-R_{\text{rough}}/R_{\text{smooth}}=\Delta R/R_0)$. The squares are the measured points for $\lambda=0.8$, 0.9, and 1.0 μ, respectively, the region where the reflectance decrease is caused primarily by optical scattering. Since we have assumed a Gaussian height distribution, the slope of the graph is -2, as predicted by Eq. (24). It is in good agreement with the experimental points, so that this rough surface does act approximately like a Gaussian surface for large relative reflectances (small values of $\Delta R/R_0$). A Gaussian surface having such relative reflectance in the 0.8–1.0-μ wavelength region would have $\rho=65.1$ Å. The corrections to the measured data at the longer wavelengths resulting from optical scattering may then be calculated from Eq. (24), and these corrected values are plotted as circles in Fig. 6 for wavelengths from 2–26 μ. For wavelengths of 4 μ and longer, the corrections are less than 0.0005, and even at 2 μ the correction is only 0.0017. The solid curve in Fig. 6 is obtained from the solid and long dashed curves in Fig. 5. Note that the circles agree closely with the calculated curve, showing that for this particular rough surface the magnitude of the decrease in reflectance between rough and smooth samples is in agreement with that predicted by theory on going from $p=1$ to $p=0$. All rough samples showed

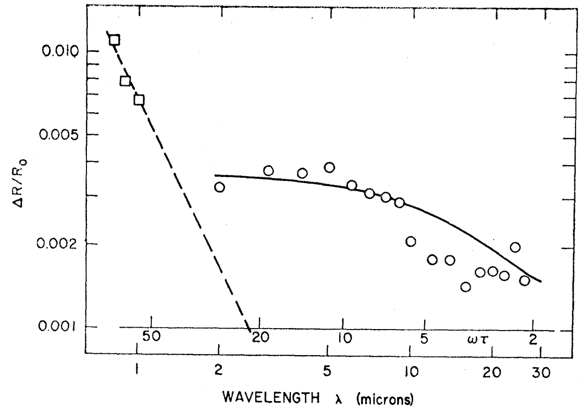

FIG. 6. Values of $(R_{\text{smooth}}-R_{\text{rough}})/R_{\text{smooth}}$ for silver. The squares are measured joints which fall on the dashed line for which $\rho=65.1$ Å rms. The circles are measured values which have been corrected for optical scattering. The solid curve was calculated from the anomalous skin effect theory using values of R for $p=1$ and $p=0$ from the solid and long dashed curves in Fig. 5.

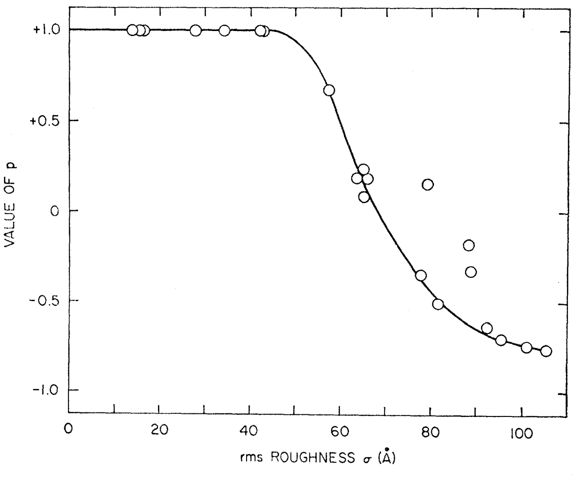

FIG. 7. Values of p for silver films of various roughnesses. When $p=1$ there is no difference between reflectances of rough and smooth samples; when $p=0$ the measured $\Delta R/R_0$ agrees with the value predicted by theory; the $p<0$ values mean that the measured differences are larger than the predicted values.

a nearly constant value of $\Delta R/R_0$ in the wavelength range from 2–28 μ, but the magnitude of $\Delta R/R_0$ varied from 0.32 to 1.76 times the value given by the solid line.

Figure 7 shows the average measured values of p obtained for the rough surfaces plotted as a function of rms surface roughness. To obtain the average value of p, the ratio between $(\Delta R/R_0)_{\text{meas}}$ and $(\Delta R/R_0)_{\text{calc}}$ was determined for each of the 17 measured points between 2 and 26 μ after they had been corrected for optical scattering. The quantity p was obtained by taking 1 minus this ratio. For example, if $(\Delta R/R_0)_{\text{meas}}/(\Delta R/R_0)_{\text{calc}}$ was 1.76, $p=1-1.76=-0.76$. Theoretically, of course, $0\leq p\leq 1$. However, for roughness larger than about 65 Å rms, the measured reflectance decrease was larger than the value predicted for p going from 1 to 0. We also found that for roughnesses less than 45 Å rms, the reflectances of the rough and smooth samples were indistinguishable in the infrared. The transition from $p=1$ to $p=0$ was quite abrupt, and occurred in the roughness range from 45–65 Å, about an order of mangitude larger than the value of 4.2 Å calculated from simple diffraction theory. Furthermore, the reflectance continued to decrease throughout the roughness range where measurements were made, also in contradiction to theoretical predictions. In order to show that the continued decrease in reflectance was not caused by a reaction between the calcium fluoride and silver films, some of the roughest samples were first overcoated with aluminum before the silver film was applied. When measured relative to a silvered optical flat which had first been coated with aluminum, these samples had the same relative reflectance as the silver-coated calcium fluoride samples.

CONCLUSIONS

The measured infrared reflectance of silver films evaporated in ultrahigh vacuum on supersmooth substrates is in excellent agreement with the anomalous skin effect theory assuming $p=1$, and in even better agreement with the simple Drude theory. For $\omega\tau<15$ the discrepancy between theory and experiment is less than 0.001, and, if a small additional term is included for electron-electron collisions, the data fit the theory for $\omega\tau<50$. The theoretical curves were calculated from values of the dc conductivity and relaxation time obtained from electrical measurements on films prepared in the same evaporations as the optical samples. No optical data were used to fit the curves to the experimental data. The electrical data were in approximate agreement with data for silver films reported in the literature, from which it had been concluded that $p\simeq 0$ for silver. Present results, however, suggest that the observed variation in resistivity with film thicknesses does not arise from diffuse electronic reflection at the air-metal interface.

The anomalous skin effect theory predicts that if $p=1$ for a very smooth surface, by making the surface rougher, the infrared reflectance should decrease until $p\simeq 0$. This prediction has been verified for silver. The roughness at which the transition occurs, however, is about an order of magnitude larger than the value calculated from simple diffraction theory, and lends support to Greene's conclusion that p is not the simple quantity which it is usually assumed to be. The transition from $p=1$ to $p=0$ is quite abrupt, occurring in the roughness range 45–65 Å rms. It seems probable that bulk samples used in anomalous skin effect measurements would have roughnesses of this order or larger, so that for these samples one would expect to find $p\simeq 0$, in agreement with published results.

The measured difference between the infrared reflectance of rough and smooth silver samples was as much as 76% larger than that predicted by theory, and was continuing to increase slightly for the roughest surfaces measured. These observations are as yet unexplained. For the smooth surfaces, however, the experimental results are in excellent agreement with theory, and suggestions that the theory must be modified to fit experimental results appear, at least for silver, to be based on inadequate sample preparation or measurement techniques.

Note added in proof. The dc measurements recently reported by K. L. Chopra and M. R. Randlett [J. Appl. Phys. **38**, 3144 (1967)] can also only be fitted to the standard theory by assuming $p<0$. Possibly the effect, which is found both at optical frequencies and at dc, is related to the presence of a thin surface film on the metal, but more work will be required to understand this question. The origin of Eq. (21) as a limiting case for reflection of conduction electrons from a rough surface is also discussed in a recent paper by S. B. Soffer [J. Appl. Phys. **38**, 1710 (1967)].

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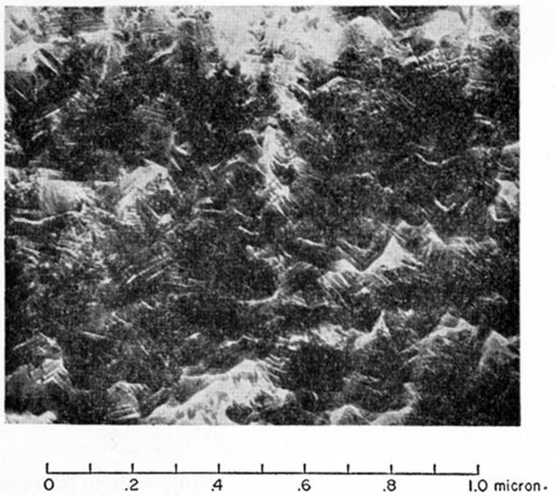

FIG. 4. Electron micrograph of a calcium fluoride film. Note that detail of the order of $0.01\ \mu$ (100 Å) can be seen.