

Interpretation of the Optical Properties of Metal Surfaces

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The surface optical properties of the metals Ag, Au, Cu, Pt, Ir, and Ni in the infrared are shown to obey a simple generalized form of the Drude formula for the free electron theory, but involving two types of free electrons. If the surface optical constants are not anomalous, this procedure may be interpreted as a source of information on the density and relaxation times of free electrons in different overlapping energy bands. The evidence for and against anomalous surface optical constants is reviewed and it is concluded that the optical constants in the interior are the same as those measured on the surface.

I. INTRODUCTION AND MATHEMATICAL FORMULATION

IN 1900 Drude¹ proposed a formula for the optical properties of metals based on the postulated existence of two kinds of free charge carriers. In 1904 Drude² abandoned this formulation since it seemed inconsistent with the electron theory which was being developed at that time. He then restricted the charge carriers to one kind. Since that time it has become evident that Drude's restricted formula may be used with only limited success and does not bring optical data into harmony with data for dc conductivity unless the optical properties of the interior are assumed to be different from those derived from reflection experiments on the surface.

It will be shown that Drude's more general formula does apply without limit to the free electron contribution to optical properties in all metals which have been studied, and that there need be no essential difference between the optical properties of the surface and those of the interior to be consistent with the dc conductivity.

Since quantum mechanics and the exclusion principle were then unknown, Drude could not have guessed that electrons in different Brillouin zones can behave differently, nor could he have suspected the existence and important function of "holes." Nevertheless, the properties which he ascribed in his earlier paper to positive and negative "ions" show a remarkable resemblance to modern ideas about holes and electrons. The parallel modern interpretation of conductivity of transition metals was proposed by Mott.³ Mott recognized that both *s*-electrons and *d*-electrons are of importance for the conductivity of transition metals. The present work extends Mott's interpretation to optical properties and indicates that even nontransition metals may have more than one type of free electron.

The Drude formula gives the complex dielectric constant, K , as a function of frequency or wavelength. The complex dielectric constant is the square of the complex index of refraction.

$$K \equiv [n(1 - i\kappa)]^2 \equiv K' - iK'' \quad (1)$$

The real and imaginary parts of K are, respectively,

$$\begin{aligned} K' &= n^2(1 - \kappa^2), \\ K'' &= 2n^2\kappa. \end{aligned} \quad (2)$$

In our notation the Drude formula may be written

$$K = K_\infty - i \frac{\sigma_\infty \lambda}{2\pi c \epsilon_0} - \frac{\lambda^2}{2\pi c \epsilon_0} \left(\frac{\sigma_1}{\lambda_1 - i\lambda} + \frac{\sigma_2}{\lambda_2 - i\lambda} \right). \quad (3)$$

In Eq. (3), λ is the wavelength in meters, σ_1 and σ_2 are components of conductivity in ohms⁻¹ m⁻¹ due to the two different kinds of charge carriers, and λ_1 and λ_2 are the corresponding wavelengths of relaxation. With these units, the value of $2\pi c \epsilon_0$ is 0.01668. K_∞ represents the contribution of "bound" electrons at long wavelengths compared to their wavelengths of resonance. σ_∞ has no theoretical foundation, but is inserted in the equation because it is useful in describing certain deviations from theory in imperfect metal films.

The dc conductivity, σ_0 , may be derived from Eq. (3) by the relation

$$\sigma_0 = \lim_{\lambda \rightarrow \infty} (i2\pi c \epsilon_0 K / \lambda) = \sigma_1 + \sigma_2 + \sigma_\infty. \quad (4)$$

It is found not only that Eq. (3) gives an adequate description of the optical properties of all metals which do not have resonance frequencies for bound electrons in the visible or infrared region, but also that it may be reduced to even simpler approximate forms. In some metals both λ_1 and λ_2 are substantially greater than the wavelengths at which data are reported. In other metals only λ_2 is large. These conditions correspond to the two special cases summarized below.

Case I: $\lambda_1^2, \lambda_2^2 \gg \lambda^2$

$$K \cong K_\infty - i \frac{\sigma_\infty \lambda}{2\pi c \epsilon_0} - \frac{\lambda^2}{\lambda_a \lambda_b} \frac{\sigma_1 + \sigma_2}{2\pi c \epsilon_0} (\lambda_b + i\lambda), \quad (5)$$

where

$$\lambda_a = \frac{(\sigma_1/\lambda_1) + (\sigma_2/\lambda_2)}{(\sigma_1/\lambda_1^2) + (\sigma_2/\lambda_2^2)}; \quad \lambda_b = \frac{\sigma_1 + \sigma_2}{(\sigma_1/\lambda_1) + (\sigma_2/\lambda_2)}$$

Note that $\lambda_1 < \lambda_a < \lambda_b < \lambda_2$.

Case II: $\lambda_2^2 \gg \lambda^2$

$$K \cong K_\infty - i \frac{\sigma_\infty \lambda}{2\pi c \epsilon_0} - \frac{\lambda^2}{2\pi c \epsilon_0} \left[\frac{\sigma_1}{\lambda_1 - i\lambda} + \frac{\sigma_2(\lambda_2 + i\lambda)}{\lambda_2^2} \right]. \quad (6)$$

¹ P. Drude, *Physik. Z.* **1**, 161 (1900).

² P. Drude, *Ann. Physik* **14**, 936 (1904).

³ N. F. Mott, *Proc. Roy. Soc. (London)* **A153**, 699 (1936).

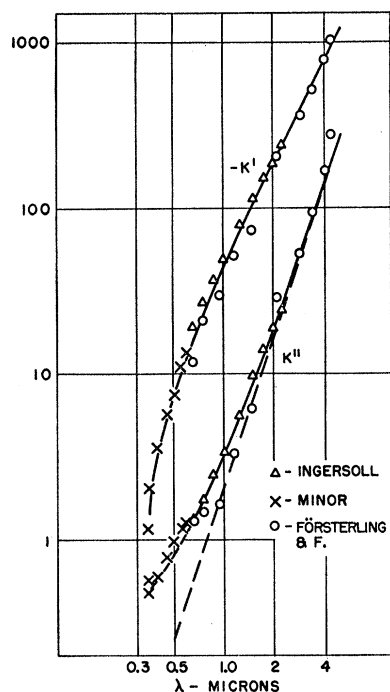


FIG. 1. Surface dielectric constant of silver.

II. COMPARISON WITH EXPERIMENT

Years ago, Meier⁴ determined the resonance frequencies of the so-called "bound" electrons in several metals. In silver he found the longest wavelength of resonance at about 0.27μ . In gold a resonance was found at about 0.37μ and in copper at about 0.50μ . Equation (5) may be used successfully at wavelengths greater than roughly twice these values.

Of these three metals, silver has the widest range of wavelength free of resonances and is probably the metal most frequently studied. Figure 1 shows data for the complex components of the optical dielectric constant of silver. The smooth curves are calculated from Eq. (5) using the parameters listed in Table I, with the exception of σ_∞ which is $0.019 \times 10^6 \text{ ohm}^{-1} \text{ m}^{-1}$. The data in the infrared are from Foersterling and Freedericksz⁵ and Ingersoll.⁶ The data of Minor⁷ are used in the visible range. Figure 1 is plotted on logarithmic coordinates, according to which $(-K')$ and K'' should follow straight lines with slopes of two and three respectively, if in Eq. (5) the parameters K_∞ and σ_∞ are omitted. The deviations from straight lines are attributable to the nonvanishing values of K_∞ and σ_∞ . The straight line asymptote for K'' is shown dashed in the figure.

More recent data for silver obtained by Schulz⁸ and Schulz and Tangherlini,⁹ which had not been published

when Fig. 1 was drawn, indicate values of $(-K')$ which coincide with the curve in Fig. 1 in agreement with the older data. The new data for K'' are different, however, in that they coincide with the dashed straight line instead of the curve in the wavelength range 0.5 to 0.95 micron. Schulz and Tangherlini stressed the importance of careful annealing of their metal films and they measured the reflectivity from the glass-metal interface which was presumably free of contamination by the atmosphere. Our conclusion from these data is that σ_∞ does vanish, as it should, on a suitably prepared surface. Conversely, a nonvanishing σ_∞ may be taken as a possible indication of surface defects. σ_∞ appears to be more sensitive to surface defects than are the other parameters in the equation.

The situation in gold and copper is somewhat similar to that observed in silver except that there is more scatter in the classical data. It should be noted that all three metals are very difficult to measure in the important infrared range because of their high reflectivities. The values of λ_a , λ_b , and K_∞ for gold and copper shown in Table I were calculated from the data of Schulz and Tangherlini which also indicate that σ_∞ vanishes for these metals. This table also lists representative values of the dc conductivity, σ_0 , of these metals at room temperature taken from the Landolt-Bornstein¹⁰ tables.

In the Drude formula for one type of free electron [obtained from Eq. (3) by putting $\sigma_2 = \sigma_\infty = 0$] one finds that $K'' > (-K')$ when $\lambda > \lambda_1$, neglecting the effect of K_∞ . In this range of wavelength $(-K')$ increases only very slightly with increasing wavelength. In the metals platinum, iridium, and nickel, $K'' > (-K')$ while $(-K')$ changes much more than could be explained by the simple formula. The data for these metals can be accounted for only under the assumption that there are two relaxation wavelengths, in this case as given by Eq. (6). In Eq. (6), σ_1 and σ_2 appear in different terms so that these parameters may be determined independently. On the contrary, Eq. (5) contains only the sum of these parameters. By fitting experimental data to Eq. (6), one can find actual values of σ_1 and σ_2 as well as λ_1 and λ_2 .

A graphical method has been found most satisfactory in the evaluation of numerical values of parameters in Eq. (6). The graphical analysis is based on a family of standard curves which show at a glance how a change in any one of the parameters would affect the shape of the resulting curves. Figures 2, 3, and 4 show the ex-

TABLE I. Parameters derived from optical data.

Metal	$\lambda_a (\mu)$	$\lambda_b (\mu)$	K_∞	$\sigma_0 \times 10^{-6}$ ($\text{ohm}^{-1} \text{ m}^{-1}$)
Ag	23.0	84.	4.6	60.7
Au	16.7	59.	~5	43.2
Cu	22.4	74.	~6	58.0

⁴ W. Meier, Ann. Physik 31, 1017 (1910).

⁵ K. Foersterling and V. Freedericksz, Ann. Physik 40, 201 (1913).

⁶ L. R. Ingersoll, Astrophys. J. 32, 282 (1910).

⁷ R. S. Minor, Ann. Physik 10, 581 (1903).

⁸ L. G. Schulz, J. Opt. Soc. Am. 44, 357 (1954).

⁹ L. G. Schulz and F. R. Tangherlini, J. Opt. Soc. Am. 44, 362 (1954).

¹⁰ Landolt-Bornstein, *Physikalisch-Chemische Tabellen* (Springer-Verlag, Berlin, Germany, 1923-36), Vol. 2 and Suppl.

perimental data for platinum, iridium, and nickel. These data include the work of Lauch,¹¹ von Wartenburg,¹² Quincke,¹³ and Tool¹⁴ in addition to those sources already mentioned. The parameters used in calculation of the curves in these figures are listed in Table II along with the dc conductivity. Some of the parameters which could not be determined uniquely by the graphical method are either omitted or enclosed in parentheses.

Iron is an exception to the above formulas since it has a resonance frequency in the visible range. The data for iron are shown in Fig. 5 along with a smooth curve calculated according to Eq. (6). The deviations from the smooth curve centered at about 0.57μ are characteristic of a resonance such as is usually attributed to bound electrons. In this case it is possible that the resonance may be magnetic in origin. A similar resonance is observed in cobalt at around 1.35μ .

III. INTERPRETATION OF RESULTS

If one considers the electronic energy diagram for copper as calculated by Krutter,¹⁵ it is clear that in the solid metal there is an overlapping of the $4s$ and $4p$

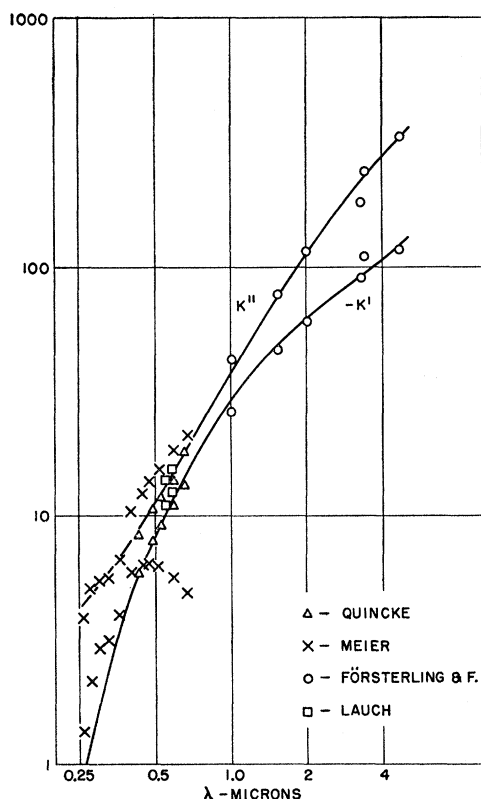


FIG. 2. Surface dielectric constant of platinum.

¹¹ K. Lauch, Ann. Physik (4), 74, 55 (1924).

¹² H. von Wartenburg, Verhandl deut physik Ges. 12, 105 (1910).

¹³ G. Quincke, Poggend. Ann. Jubelband 336 (1874).

¹⁴ A. Q. Tool, Phys. Rev. 31, 1 (1910).

¹⁵ H. M. Krutter, Phys. Rev. 48, 664 (1935).

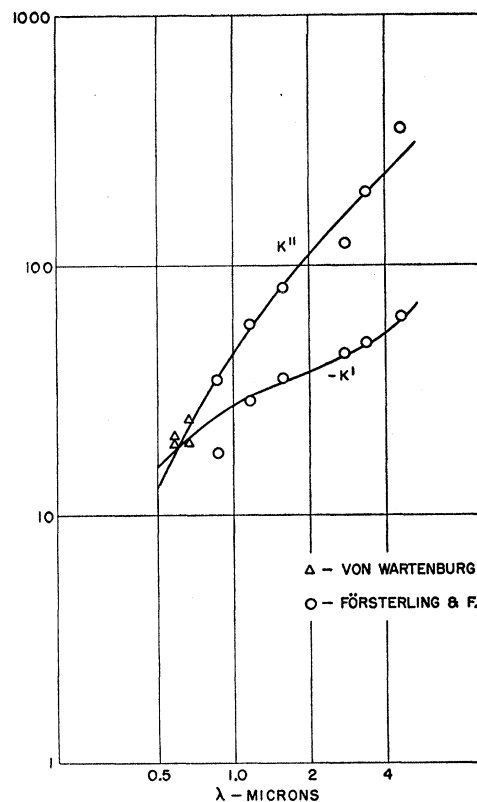


FIG. 3. Surface dielectric constant of iridium.

bands and that the Fermi level falls in this overlapping range. According to this model both $4s$ and $4p$ electrons will contribute to the conductivity. Free electrons in these different bands would be expected to have different effective masses and scattering probabilities or relaxation wavelengths. Silver and gold are known to have similar electronic properties as compared with copper; therefore, one might expect a similar energy band model to apply to these metals. In silver the expected overlapping bands would be $5s$ and $5p$ and in gold, $6s$ and $6p$. The fact that the two-electron model appears to give a better interpretation of the experimental data than the one-electron model tends to support the conclusion that both s - and p -electrons contribute to the conductivity in these metals. The existing data do not allow separate determination of λ_1 , λ_2 , σ_1 , and σ_2 ; however, it is evident that these can be determined by conducting experiments at longer wavelengths.

In platinum and iridium the situation should be, and is, quite different, since these metals have unfilled d -orbitals; the overlapping occurring between the $5d$ - and $6s$ -bands. In nickel $3d$ - and $4s$ -states would be involved. The values obtained for λ_1 and σ_1 in these metals are attributed to d -states, while the values for λ_2 and σ_2 are attributed to s -states. The small values of λ_1 are interpreted to indicate that the charge carriers in d -states have a much greater probability of scattering

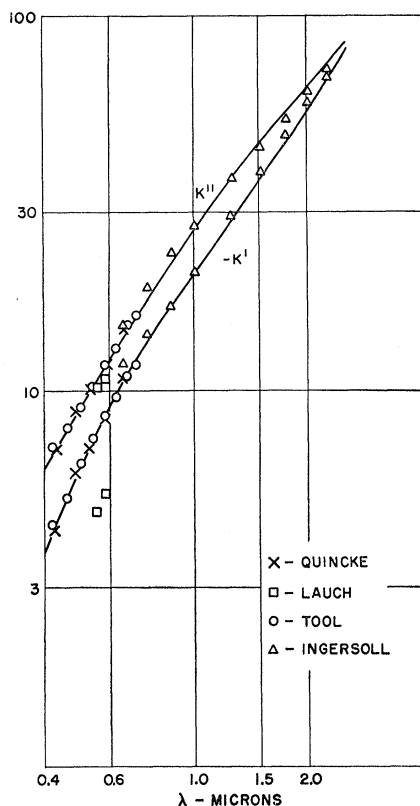


FIG. 4. Surface dielectric constant of nickel.

than do those for either *s*- or *p*-states. For these transition metals, one may use the experimentally derived values of λ_1 and σ_1 in a calculation of the effective number, n_1 , of electrons or other charge carriers in the *d*-state. This calculation is based on the classical relation

$$n_1/n_a = 2\pi c m_1 \sigma_1 / n_a e^2 \lambda_1, \quad (7)$$

where n_a is the number of atoms per unit volume, c is the velocity of light, e is the electronic charge, and m_1 is the effective electronic mass. This equation is not capable of determining both n_1 and m_1 , but if one assumes that m_1 is the rest mass of an electron in free space, then one obtains a representative value for n_1 . The values of n_1/n_a for platinum, iridium, and nickel calculated according to this convention are shown in Table III.

Platinum and iridium have similar electronic configurations except that iridium has one less electron. In view of this, it is interesting that iridium has a noticeably greater number of charge carriers in the *d*-state. Since the metal with fewer electrons has the greater number of charge carriers, the latter may be identified as holes. This is reasonable since the *d*-band has room for ten electrons and is nearly filled. The charge carriers associated with the *s*-states are believed to be electrons. Most of the conductivity is due to these

s-electrons since they have so much greater lifetime than the *d*-holes.

IV. ANOMALOUS SURFACE LAYER

Until now it has been generally believed that the optical properties of metals are influenced by an anomalous surface layer. This layer has been discussed at length by several authors.¹⁶ The analysis presented here appears to cast some doubt as to whether such a surface layer does have any significant effect on the optical properties of metals in the infrared at ordinary temperatures. Accordingly, it is relevant to review the evidence for and against the anomalous surface optical constants resulting from such a layer.

The point in dispute is whether the optical constants determined from surface measurements are valid for points in the interior of the metal. To settle this point properly, one should compare experimental data for the optical constants in question. The surface constants are well known for a number of metals, but data for the interior as reported in the literature are relatively meager. However, these data do definitely support the view that the optical constants of the interior are the same as those of the surface.

TABLE II. Parameters derived from optical data.

Metal	$\lambda_1(\mu)$	$\lambda_2(\mu)$	K_∞	$\sigma_1 \times 10^{-6}$ (ohm ⁻¹ m ⁻¹)	$\sigma_2 \times 10^{-6}$ (ohm ⁻¹ m ⁻¹)	$\sigma_\infty \times 10^{-6}$ (ohm ⁻¹ m ⁻¹)	$\sigma_0 \times 10^{-6}$ (ohm ⁻¹ m ⁻¹)
Pt	1.27	205.	2.4	1.03	8.22	0.25	9.5
Ir	0.58	724.	...	1.02	15.4	...	16.4
Ni	0.70	44.	(2.7)	0.45	7.90	(0.15)	8.5
Fe	0.39	75.	(1.15)	0.24	9.52	(0.24)	10.0

One of the first suggestions that the surface optical constants might be anomalous came from application of the Drude one-electron formula [$\sigma_2 = \sigma_\infty = 0$ in Eq. (3)] to copper-like metals. If one neglects K_∞ and restricts the range of wavelength so that $\lambda^2 \ll \lambda_1^2$ one obtains the following relation between conductivity and optical constants from the one-electron formula

$$\sigma_0 \cong \pi c \epsilon_0 (n\kappa)^3 / \lambda n. \quad (8)$$

If one uses surface optical constants, this formula gives values of conductivity which are only about 0.3 of the observed dc conductivity of the solid metal for each of the three metals silver, gold, and copper. Therefore, if the formula is valid for the interior, $n\kappa$ must be about 49% larger in the interior or n must be 70% smaller than the value measured on the surface. The two-electron formulation does not give rise to such a difference.

Recent experiments of Schulz¹⁷ indicate that, for the metals he studied, the extinction coefficients, $n\kappa$, of the

¹⁶ A. B. Pippard, Proc. Roy. Soc. (London) **A191**, 385 (1947); **A203**, 98 (1950); R. G. Chambers, Nature **165**, 239 (1950); Ph.D. dissertation Cambridge, 1951 (unpublished); Physica **19**, 365 (1953); E. H. Sondheimer, Advances in Phys. **1**, 1 (1952); R. B. Dingle, Physica **19**, 311, 729-36 (1953).

¹⁷ L. G. Schulz, J. Opt. Soc. Am. **44**, 540 (1954).

interior were not much, if any, different from those of the surface. Schulz observed the transmission through films of varying thickness and from these data calculated separate values of $n\kappa$ for the surface and for the interior. He also determined $n\kappa$ for the surface independently by reflection. Observed differences up to about 15 percent between surface and interior values of $n\kappa$ were much too small to reconcile the simple Drude formula with the dc conductivity. These differences are not regarded as significant in the present discussion, and on this basis Schulz's experiments may be interpreted to signify that the interior and surface values of the extinction coefficient are substantially the same.

Schulz did not determine the real component, n , of the index of refraction of the interior. However, this property was measured many years ago by Kundt¹⁸ using metal wedges. With the exception of silver, Kundt's interior results for "white" light are in very good agreement with the surface indices reported by others. Kundt's interior value of n for Ag is several times higher than the latest surface value of Schulz and Tangherlini.⁹ Kundt's value for Ag is probably in error since the discrepancy in the one-electron formulation is even greater using his value. There is better agreement between Kundt's interior values and the surface values

TABLE III. Analysis of charge carriers.

Metal	n_1/n_a
Pt	0.79(5 <i>d</i>)
Ir	1.64(5 <i>d</i>)
Ni	0.47(3 <i>d</i>)

of n for the metals Pt and Ni than for copper-like metals. This would be expected since Kundt did not use monochromatic light, and the values of n for the metals Pt and Ni are not such critical functions of wavelength.

The evidence for anomalous surface optical constants is not based on a direct comparison of the surface constants with those of the interior but on a theoretical interpretation of other properties of metals. Furthermore, the theory of the anomalous surface layer is in internal disagreement when applied to different experiments. For example, Andrew¹⁹ obtained the value $\sigma_0/l = 4.5 \times 10^{22}$ Gaussian units for the ratio of the conductivity to the electronic mean free path in tin as derived from measurements of the dc conductivity of thin foils at low temperatures. Chambers¹⁶ obtained the value 8.6×10^{22} for the same ratio on the basis of microwave resistance measurements, also at low temperatures. This difference appears to be well outside the

¹⁸ A. Kundt, Ann. Physik 34, 469 (1888).

¹⁹ E. R. Andrew, Proc. Phys. Soc. (London) A62, 77 (1949).

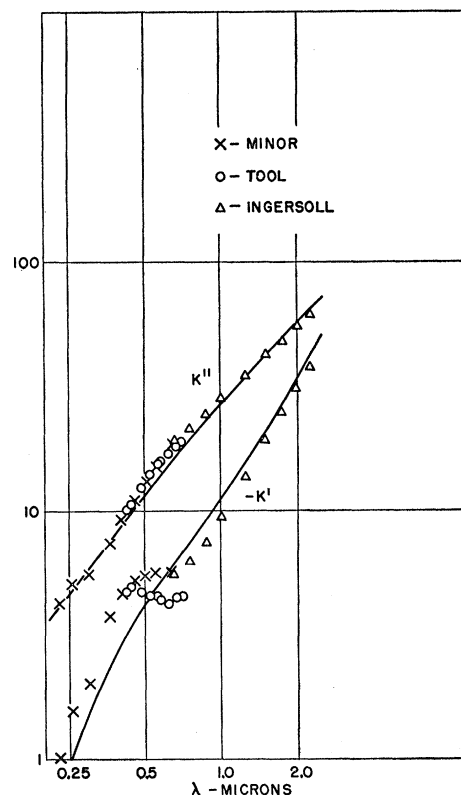


FIG. 5. Surface dielectric constant of iron (steel).

limits of experimental error; therefore, one may conclude either that the theory is deficient, or that the anomalous surface layer is less deep for microwave frequencies than for direct current—and perhaps of quite negligible depth at infrared wavelengths.

Sondheimer¹⁶ gives a method for calculating the effective conductivity of a surface layer of any given depth. Sondheimer's theory has been subjected to an extreme degree of refinement by Dingle.¹⁶ Notwithstanding these efforts, there does not seem to be any satisfactory way, analogous to Eq. (8), to calculate the dc conductivity from the surface optical constants or vice versa as long as the one-electron model is used. Nor do these theories offer any help in explaining the observed wavelength dependence of the surface optical properties of transition metals. In addition to these shortcomings it must be reckoned that the anomalous surface layer is just a theory, insofar as optical properties of metals are concerned, whereas direct experiments indicate that anomalies in the surface optical constants are either small or nonexistent at room temperature.

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