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Optical Properties of Copper

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Optical properties of solid copper have been measured in a wavelength range from 0.365 to 2.5 microns and at temperatures 90°, 300°, and 500°K. Annealed and electropolished specimens were used. Measurements were done in a vacuum of about 2×10^{-5} mm (Hg) and it was observed that the oxide film which normally forms on copper upon exposure to air could be removed by heating in vacuum to a temperature of 500°K. In the wavelength range below 0.6 micron the data confirm the well-known facts relating to a threshold for interband electronic transitions. At longer wavelengths the optical properties are determined almost entirely by free electrons. Deviations from simple theory are partly explained by the anomalous skin effect and it is concluded that the electronic collisions at the metal surface are diffuse. However, it is shown that the anomalous skin effect is not sufficient to explain the observed deviations and that a more complete interpretation ought to consider the nonspherical nature of the Fermi surface and variation of the relaxation time over this surface.

I. INTRODUCTION

The three monovalent metals Ag, Au, and Cu are often thought to be "simple" in that a number of their important physical properties are interpreted in terms of what is known as the "free electron model." These metals are also easy to handle, in contrast to the alkali metals, and for this reason many studies of their characteristics have been made. Their optical properties, especially in the red and infrared wavelength range are of interest because they are almost entirely attributed to the free electrons.

Optical experiments include the measurement of two parameters at each wavelength. These consist of the real and imaginary parts, n and $-k$, of the complex index of refraction, or the corresponding parts, K' and $-K''$, of its square which is called the complex dielectric constant. Some of the behavior of free electrons in these metals may be deduced directly from studies of optical properties. In particular, the free electrons are thought to be characterized by an average interval between collisions which is called the relaxation time. Relaxation times may be determined, in principle, by studying the way the optical properties depend on wavelength. At sufficiently long wavelengths one should expect to be able to correlate optical properties with the electrical (dc) conductivity, since both phenomena are attributed to the same free electrons.

Despite the large amount of work that has been done, there are unresolved differences in the experimental results reported for the metals Ag, Au, and Cu at room temperature, by different authors and there has been little or no work at other temperatures. Since a knowledge of the temperature dependence of optical properties is desirable in order to test theoretical predictions, the author has undertaken a thorough investigation of copper at the temperatures 90°K, 300°K, and 500°K. Of the three metals mentioned above, copper was chosen because of the ease with which it may be electropolished.

The simplest classical treatment of optical properties of metals, and the one most generally attributed to Drude, considers the free electrons to have a single relaxation time. This leads to a simple formula for the complex dielectric constant of a metal versus wavelength.

$$K=K_\infty-\frac{\sigma_0\lambda^2}{2\pi c\epsilon_0(\lambda_0-i\lambda)},\tag{1}$$

where λ is the given wavelength, σ_0 is the electrical conductivity (in mks units), K_∞ is the part of the dielectric constant not due to free electrons, c is the velocity of light, and ϵ_0 is the permittivity of space ($2\pi c\epsilon_0=0.01668$). The λ_0 is a constant related to the relaxation time, τ, by the expression

$$\lambda_0=2\pi c\tau.\tag{2}$$

Equation (1) represents an ideal case corresponding to perfectly free electrons having a spherical Fermi surface. As might be expected, this equation seldom if ever agrees precisely with experimental observations on solid metals. However, it does seem to be in accord with data on a number of liquid metals studied by Kent[1] and by Schulz.[2] There are three main reasons why Eq. (1) may fail to agree with experiment.

One reason is the existence of electronic energy states admitting transitions which influence the optical properties and yet do not provide any electrical conductivity. The electrons taking part in these transitions are called "bound" electrons and give rise to a different type of expression from that shown in Eq. (1). In paper II the author[3] made an analysis of the optical properties of nickel and tungsten which shows how the bound electron terms do modify the dielectric constant in these metals. In the case of copper, the bound electron terms seem to be important at wavelengths below 0.6 μ but not at longer wavelengths.

A second reason for not obtaining results in agreement

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[1] C. V. Kent, Phys. Rev. **14**, 459 (1919).

[2] L. G. Schulz, Suppl. Phil. Mag. **6**, 102 (1957).

[3] S. Roberts, Phys. Rev. **114**, 104 (1959).

with Eq. (1) is based on the phenomenon known as the "anomalous skin effect." In the "extreme relaxation" range of wavelength, considered here, the standard treatment may be greatly simplified. Electrons near the surface have frequent collisions at the surface and therefore have a shorter mean free path and a smaller effective relaxation time than the electrons deeper in the metal which determine the bulk electrical conductivity. Since the light waves penetrate but a very short distance into the metal, they interact only with the electrons near the surface. Therefore the observed optical properties in some cases cannot be correlated with the electrical conductivity in the manner attempted in Eq. (1) unless explicit account is taken of the reduced conductivity near the surface.

The third reason for this disagreement is that the relaxation processes for free electrons often involve more than the one relaxation time, or relaxation wavelength, indicated in Eq. (1). If the Fermi surface is nonspherical, then the effective electronic mass and relaxation time may be thought to vary from point to point on this surface. From a theoretical point of view it remains to be decided whether or not the dielectric constant of such a metal may be described by a simple equation with a finite number of terms when relaxation effects are taken into consideration. There is no doubt, however, that the experimental data so far recorded are consistent with a formula involving a small, finite number of terms having different relaxation times. For example, the author[3] showed that the optical properties of nickel could be very closely approximated by such a formula with three relaxation times.

This equation, having terms with different relaxation times, can be approached in a qualitative way by regarding the free electrons as occupying different overlapping energy bands related to the energy levels of the free atom. On certain portions of the Fermi surface certain of these atomic-like states are more important than others. The electrons in different bands, or in different parts of these bands, may be thought to have different relaxation times giving rise to additional terms like the last term in Eq. (1). Although recognized by Drude,[4] the importance of multiple relaxation times in relation to optical properties of metals seems to have been altogether disregarded by those who have written on this subject during the interval of about fifty years between Drude's work and paper I of the present author.[5]

When the optical properties of a metal do not conform with the simple formula of Eq. (1), it is not always easy to prove which of the three reasons mentioned above correctly accounts for the deviations from simple theory. It is hoped that the present work will help to clarify this problem.

II. THE ANOMALOUS SKIN EFFECT

A great deal has been written about the anomalous skin effect in different metals for various ranges of wavelength and temperature. One should note, first of all, that all of this work is based on the assumption of a single relaxation time or relaxation wavelength, so that Eq. (1) is the appropriate classical formula which serves as the starting point. The general treatment, discussed recently by Pippard,[6] may be greatly simplified if one restricts oneself to the "extreme relaxation" region of the spectrum, for which $\lambda_0/\lambda(=\omega\tau)\gg 1$. In this case Eq. (1) reduces to:

$$K=K_\infty-\frac{\sigma_0}{2\pi c\epsilon_0\lambda_0}\lambda^2-i\frac{\sigma_0}{2\pi c\epsilon_0\lambda_0^2}\lambda^3. \tag{3}$$

This equation may be thought to give the classical or "bulk" dielectric constant, but it does not often agree with the results of measurements of light reflected from the surface. Since the mean free path of electrons near the surface is shorter than that of deeper lying electrons owing to surface collisions, and since it is just this surface layer that determines the phase and amplitude of reflected light, one may obtain the appropriate formula for the measured dielectric constant by replacing σ_0 and λ_0 in Eq. (3) with other values, σ_s and λ_s, that are effective near the surface. If σ_s is less than σ_0 on account of surface collisions, then λ_s will also be less than λ_0 for the same reason and by the same factor, $1/\alpha$. The ratio σ_s/λ_s will accordingly be the same as σ_0/λ_0. However, σ_s/λ_s^2 will be greater than σ_0/λ_0^2 by the factor α. Consequently, the formula for the dielectric constant as measured at the surface may be written:

$$K=K_\infty-\frac{\sigma_0}{2\pi c\epsilon_0\lambda_0}\lambda^2-i\frac{\alpha\sigma_0}{2\pi c\epsilon_0\lambda_0^2}\lambda^3. \tag{4}$$

Assuming this equation to be correct, one can evaluate the parameters λ_0 and α from the optical data if the electrical conductivity, σ_0, is already known.

In the more rigorous treatment by Dingle,[7] the dielectric constant is in effect expanded into a series in ascending powers of λ. This series converges so rapidly in the extreme relaxation range that it is only necessary to consider terms involving the square and the cube of λ. These terms are identical with the corresponding terms in Eq. (4) if one puts

$$\alpha=1+\tfrac{3}{8}l(1-p)/\delta, \tag{5}$$

where

$$\delta=\frac{\lambda}{2\pi k}\cong\frac{\lambda}{2\pi\sqrt{-K'}},\quad (\text{assuming } -K'>K'').$$

In Eq. (5) l stands for the electronic mean free path

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

[5] S. Roberts, Phys. Rev. **100**, 1667 (1955).

[6] A. B. Pippard, Advances in Electronics and Electron Phys. **6**, 1 (1954).

[7] R. B. Dingle, Physica **19**, 311 (1953).

and δ is the skin depth for electromagnetic radiation. The parameter p denotes the fraction of electrons that are specularly reflected from the surface of the metal. Note that the skin depth, δ, is the "true" skin depth and not the "classical" skin depth for which other authors often use this same symbol. There is no ambiguity in selecting the value of K' to be used in calculating δ because K' is the same in either Eq. (3) or Eq. (4). According to Eq. (5) there is no anomaly of the skin effect, i.e., $\alpha=1$, in the "extreme relaxation" range when $p=1$; however, a different conclusion would apply at the longer wavelengths, which are not being considered here. It is most often assumed that $p=0$ and the author's experiments tend to confirm this assumption.

The skin effect is anomalous only to the extent that α differs from unity. Hence, if l is too small compared with δ, it may not be possible to distinguish any anomaly. For example, the optical properties of the liquid metals Bi, Cd, Ga, Hg, Pb, and Sn studied by Kent[1] and Schulz[2] are consistent with the value $\alpha=1$, thereby implying that l is small. Whenever α is significantly different from unity one may, in principle, determine the appropriate value of l by substituting the known values of α and δ and assuming $p=0$ in Eq. (5). The resulting value of l may be tested by comparing it with the value of the mean free path determined in other experiments. Similarly $2\pi cl/\lambda_0$ may be compared with the independently calculated value of the Fermi velocity.

Equation (4) does have the limitation that it is useless at wavelengths comparable to or greater than λ_0. However, whenever l is large enough to matter in comparison with δ, one generally finds that λ_0 is very far in the infrared compared with the wavelengths employed in the work reported here.

The foregoing treatment is based on the assumption that there is but a single relaxation wavelength. Since this is thought not to be the case, it is necessary to expand the classical formula, Eq. (1), by adding terms with different relaxation wavelengths. The more general formula is that used by the author[3] in the analysis of nickel and tungsten.

$$K=1+\sum_m \frac{K_{0m}\lambda^2}{\lambda^2-\lambda_{sm}^2+i\delta_m\lambda_{sm}\lambda}-\frac{\lambda^2}{2\pi c\epsilon_0}\sum_n \frac{\sigma_n}{\lambda_{rn}-i\lambda}. \quad (6)$$

The terms in the first summation in Eq. (6) are called "bound" electron terms, while those in the second summation are called "free" electron terms and it is the latter which correspond to the different relaxation wavelengths, λ_{rn}, referred to above. In order to account for the anomalous skin effect it may be supposed that any free electron term in Eq. (6) may be modified in the same way that Eq. (1) is modified in the discussion leading to Eqs. (4) and (5).

III. EXPERIMENTAL PROCEDURE

The apparatus shown in the Fig. 1 of paper II[3] has been modified somewhat for measurements on copper, to attain greater precision. The two main polarizing prisms P_1 and P_2 are the same; however, a new prism P_3 of the Glan-Thompson type is mounted near the light source between the collimating slit S_1 and the light chopper. The rotator of the G-T prism has two positions, for transmitting parallel and perpendicular polarization, respectively. The new prism takes over the function of the calcite crystal indicated in the figure in a different place but omitted in the modification.

The purpose of the measurement is to determine the ratio of the amplitudes, ρ or $\tan\psi$, and the phase difference, Δ, between the two components of the reflected beam corresponding to parallel and perpendicular polarization, respectively. This information may be derived from the observed ratios of transmitted intensity when the middle prism, P_1, is rotated from one selected position to another. This method of doing this is shown in Appendix I.

The square of the complex index of refraction of the metal, or its optical dielectric constant, may be determined from ψ and Δ and the angle of incidence, ϕ_1, by an exact formula which is derived from Fresnel's equations for reflection.

$$K=\sin^2\phi_1\left[1+\tan^2\phi_1\left(\frac{\cot 2\psi-i\sin\Delta}{\csc 2\psi+\cos\Delta}\right)^2\right]. \quad (7)$$

In deriving Eq. (7) it is assumed that there is a simple interface between two homogeneous optical media. If this is not the case, then it may be said that the result obtained from Eq. (7) is an apparent or effective dielectric constant, K_{eff}. The need to distinguish between K_{eff} and the true value of K arises, for example, when the surface is covered by a thin layer of transparent dielectric.

In studying the optical properties of copper one has to deal with two types of surface films. One of these consists of an amorphous layer of copper which is produced by mechanical polishing. This layer has a higher electrical resistivity and larger effective values of n and K'' than an undeformed copper surface, such as that produced by electropolishing. It is believed that the specimens used in these experiments are free of this deformed layer.

However, the dielectric film, presumably of cuprous oxide, which forms readily on any exposed copper surface, has until now been a major deterrent to the accurate measurement of the optical properties of copper. Several authors[8] have reported that this film forms either in a few minutes or gradually over a period

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[8] P. Drude, Ann. Physik **39**, 481 (1890); A. Q. Tool, Phys. Rev. **31**, 1 (1910); R. Kretzmann, Ann. Physik **37**, 303 (1940); J. F. Archard, P. L. Clegg, and A. M. Taylor, Proc. Phys. Soc. (London) **B65**, 758 (1952).

of hours. Winterbottom[9] has reported detailed studies of the surface films on copper in connection with the optical properties at 5461 A and 5780 A. He showed that the oxide films could be reduced by heating to above 460°K in hydrogen. It may be inferred from the author's success in reducing these films in a moderate vacuum and maintaining the surfaces clean that the residual gas in his system must have been largely of a reducing nature.

The method for removing the film was discovered inadvertently after the copper bar had been heated to 500°K in order to make measurements at this temperature. When cooled again to room temperature the bar seemed to have different optical constants from initial data at that temperature when its original film was intact. The reason for this change was not at first understood, but all accumulated experience since then shows conclusively that the procedure of heating to 500°K in a vacuum of about 2×10^{-5} mm (mercury) is just what is needed to get rid of the oxide film. A new film could be formed by admitting air or oxygen and the process could be repeated any number of times. The corroborating evidence will be presented in the section dealing with observations on surface films.

The copper samples were in the form of bars about $8\times5\times50$ mm in size. A bar was mounted inside a heavy copper receptacle attached under the base of a well built into the top of the vacuum chamber. The receptacle was heated by an electric heater inserted in the well and was cooled by pouring liquid nitrogen into the well. The receptacle was enclosed by a heavy copper shield with openings which could be fitted with glass windows in order to transmit the incident and reflected radiation but to exclude vapors which might become condensed on the sample at the low temperatures. The glass windows were found to introduce a significant polarization error because they were tilted 10° relative to the light path. In calculating the results a correction had to be made for the polarizing effect of the windows. When the appropriate correction was made, the results obtained using windows were in perfect agreement with those obtained without windows.

The copper used in these experiments was obtained from two sources. Some of the samples were machined from $\frac{3}{8}$-in. diameter rod, supposedly of 99.999% purity, supplied by American Smelting and Refining Company. Other samples were prepared from zone-refined copper which was purified in this laboratory by F. H. Horn. In each case the machined copper bars were annealed in hydrogen at 930°C and were then electropolished in a phosphoric acid solution. No mechanical polishing was ever done. The crystal grains in the AS&R Company samples were of the order of 0.1 mm across, while the width of the crystals in the zone refined copper was generally greater than 1 mm, and they were as long as the area under study.

The electropolishing was continued long enough to remove the tool marks and produce a smooth, bright surface, though not perfectly flat. The angle of incidence used in these experiments, 80°, was small enough so that no trouble was encountered owing to lack of flatness of the surfaces being studied.

IV. OBSERVATIONS OF SURFACE FILMS

It seems appropriate to describe first the results of observations of the growth and reduction of surface films on the copper samples. These studies were carried out at the single wavelength 1.0 micron and at room temperature. The detailed results obtained on clean surfaces at other wavelengths and temperatures will be considered later. This is not the order in which the experiments were done, but it seems logical to present them this way since the validity of the other data depends on an adequate control of the surface film.

On seven separate occasions measurements at 1.0 micron were made soon after cooling to room temperature from 500°K. The resulting read and imaginary parts of the optical dielectric constant fall in the third quadrant of an Argand diagram and are so plotted on an expanded scale in Fig. 1. Three of these points, shown by circles, indicate tests on a sample of the high purity copper supplied by American Smelting and Refining Corporation (ASR). The other four points, shown by triangles give the results of measurements on a sample of zone refined copper (ZRC). There is no significant difference in results obtained on copper from the two different sources.

The average of the seven points is indicated in Fig. 1 by a square, and is assumed to represent the preferred value for the complex dielectric constant of clean copper. The differences which are observed among the seven points are thought to be entirely attributable to limitations of the measuring equipment. The ability to reproduce measurements to this same degree of accuracy has been maintained consistently in all the work to be reported.

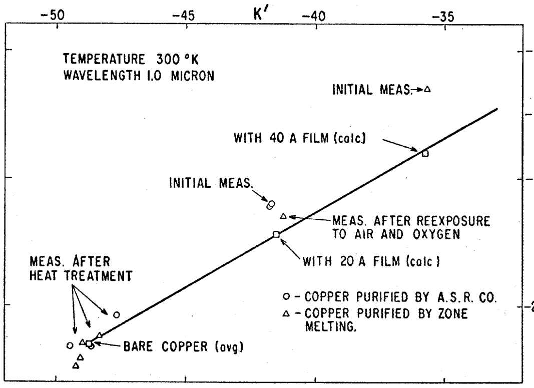

Fig. 1. Argand diagram showing effect of surface films on measured dielectric constant ($K'-iK''$).

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[9] A. B. Winterbottom, Kgl. Norske Videnskab. Selskabs Fosh. Skrifter No. 1, 95 (1955).

Two other points, also shown by squares in Fig. 1, correspond to the "effective" dielectric constants that would be measured in the author's apparatus on a copper surface covered by transparent dielectric films with an index of refraction 2.5 and thicknesses of 20 A and 40 A, respectively. These points were calculated on the basis of Drude's[10] "exact" formulas, which are summarized in more modern notation in Appendix II. Other points shown in Fig. 1 denote the initial measurements on two ASR samples and on one ZRC sample. The initial film on the ZRC sample was evidently much thicker than that on the ASR samples.

When the clean ZRC sample was again exposed to air and oxygen, it developed another surface film. The effective dielectric constant after this treatment is represented by one more point in Fig. 1. It is evident from this figure that both the real and imaginary parts of the observed dielectric constant varied in a manner that is reasonably consistent with the calculated effect of dielectric films of varying thickness.

The observed value of $\cos\Delta$ is a sensitive indication of the surface film. When the values of $\cos\Delta$ for the three points indicated by squares in Fig. 1 are plotted versus film thickness, one obtains a straight line which provides a means of estimating film thickness directly from $\cos\Delta$ without going through a long calculation. This method of determining film thickness assumes that the film is cuprous oxide with an estimated index of refraction of 2.5.

The first steps preparatory to admitting air were to turn off the diffusion pump and allow it to cool and to thaw out the liquid nitrogen trap between the diffusion pump and the vacuum chamber. While thawing out the trap, a momentary pressure rise to about 200 microns was observed, which was attributed to water vapor. According to the measured value of $\cos\Delta$, this procedure deposited a film of average thickness 1.4 A on the copper surface, still assuming an index of refraction 2.5. An equivalent change in $\cos\Delta$ would be produced by a film about 2.6 A thick having the index of refraction of water.

TABLE I. Cosine of retardation angle and inferred film thickness for various conditions.

History of surface	$\cos\Delta$	d(A)
Clean copper	−0.232	0
After 1 day at 2×10^{-5} mm (Hg)	−0.217	3.3
After 2 months at 10^{-2} mm (Hg) (treatment included thawing trap)	−0.210	5.3
After reheating in vacuum	−0.232	0
After thawing trap	−0.225	1.4
After 5 min in air	−0.198	8.5
After 35 min in air	−0.190	10.7
After 1 hr in air	−0.185	11.6
After 2 hr in air	−0.178	13.8
After 3 hr in air	−0.173	15.4
After 6 hr in air	−0.167	17.0
After 22 hr in air	−0.153	20.4
After 22 more hr in O_2	−0.146	22.4
After reheating in vacuum	−0.234	0
After thawing trap again	−0.219	2.7
After 5 min in O_2	−0.170	16.2

$\lambda=1$ micron, Temperature 300°K

TABLE II. Optical properties of copper at 90°, 300°, and 500°K.

	90°K		300°K		500°K	
λ	$-K'$	K''	$-K'$	K''	$-K'$	K''
0.365	3.35	4.36	3.14	4.44	2.01	3.88
0.405	4.15	4.77	4.08	4.93	3.12	4.42
0.436	4.98	5.10	4.91	5.27	4.06	4.67
0.50	6.68	5.78	6.69	5.74	5.77	5.32
0.55	6.51	4.40	6.76	4.30	6.22	4.06
0.578	8.06	1.20	8.26	1.88	7.48	2.28
0.60	11.08	0.65	10.78	0.98	9.60	1.38
0.65	15.52	0.62	15.28	0.84	14.00	1.00
0.75	23.95	0.78	23.85	1.01	22.38	1.32
1.0	48.19	1.48	48.05	2.04	46.10	2.68
1.5	114.3	4.03	114.0	5.69	110.4	7.51
2.0	205.7	8.75	205.2	12.38	198.4	16.29
2.5	311.0	15.53	310.8	22.02	299.6	28.83

The next step was to admit air from the room for five minutes and then to pump it right out again. This was done during a period of rather high relative humidity. After this exposure the estimated film thickness was 8.5 A. Air was then readmitted and the measurements were repeated from time to time. Table I shows the results of these measurements as well as other experiments on the same specimen of copper.

The data tend to show that the clean copper surface had a special affinity for one or two molecular layers of water or oxygen. At the pressure 2×10^{-5} mm (Hg) it took about a day for the first molecular layer to form. It is not known what gases were present in the vacuum chamber but it is possible that the partial pressure of oxygen may have been a very small fraction of the total. After the formation of one or two molecular layers the reaction proceeded at a much slower rate. In fact the reaction stopped completely at this point when the copper was just maintained in a rough vacuum of 10^{-2} mm (Hg). The faster rate at which the first molecular layer formed is cited as evidence that the surface was relatively clean to start with.

V. OPTICAL CONSTANTS OF COPPER

The results of measurements of K' and K'' at 90°, 300°, and 500°K are given in Table II. The data at 300°K were obtained by averaging four series of measurements, using samples of copper from the two different sources with and without the internal windows. Before each series the copper had been heated in vacuum to 500°K. However, the measurements were not always done immediately after returning to room temperature. Since there was time for a detectable surface film to form, the average of the four measurements at 1.0 micron, $K=-48.05-i2.05$, did not quite agree with the result, $K=-48.65-i2.15$, obtained by averaging the seven measurements quoted earlier. Although this difference is outside the experimental limits of repro-

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[10] P. Drude, Ann. Physik **36**, 865 (1889).

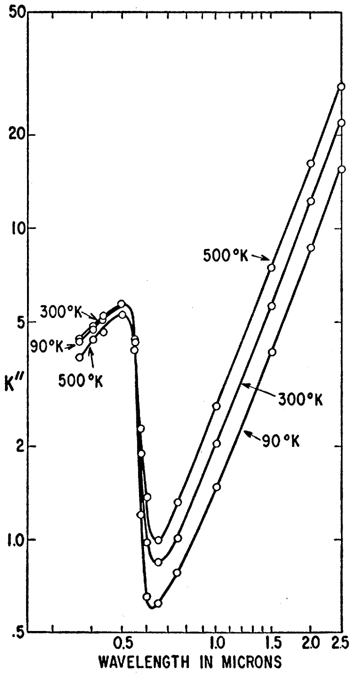

FIG. 2. Imaginary part of dielectric constant of copper at different temperatures.

ducibility, the author did not consider it sufficiently important to make a correction for it or to repeat the measurements under better controlled conditions.

The sets of data in Table II at 90°K and 500°K were each obtained by averaging two series of measurements. The actual temperatures of the low temperature measurements were 85°K and 95°K, but no difference in optical properties was observed at these two temperatures. Before and after each series of measurements a check of optical properties was made at room temperature for the wavelength 1.0 micron. In this way it was ascertained that no irreversible change had occurred during the temperature cycle.

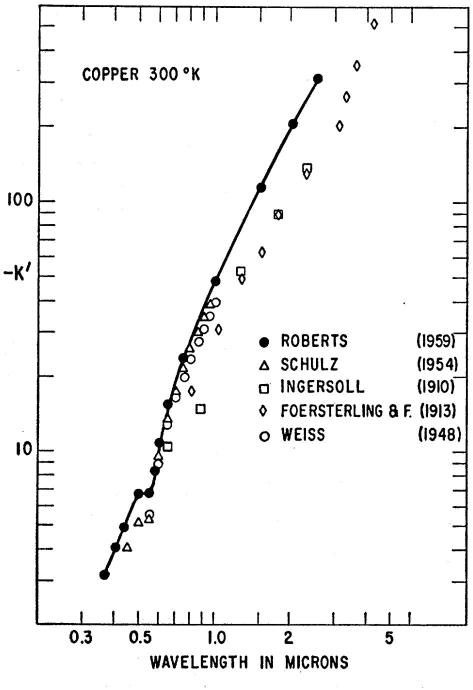

FIG. 3. Real part of dielectric constant of copper at 300°K.

The data for K'' at the three temperatures are plotted in Fig. 2. The differences in the values of K' at the three temperatures are so small over most of the wavelength range that it is difficult to distinguish between them on a graph. However, the values obtained by the author for K' at room temperature are shown in Fig. 3 in comparison with the earlier data reported by Ingersoll,[11] Foersterling and Freedericksz,[12] Weiss,[13] and Schulz.[14] Figure 4 shows a similar comparison of data for K''. Since no two of the earlier authors agree with each other, it is interesting to note that the new results are in remarkably close agreement with those reported by Schulz in the red and infrared wavelength range. The reasons for better agreement with Schulz seem to be that he both recognized the need for an annealing treatment and found a way to avoid the oxide surface film.

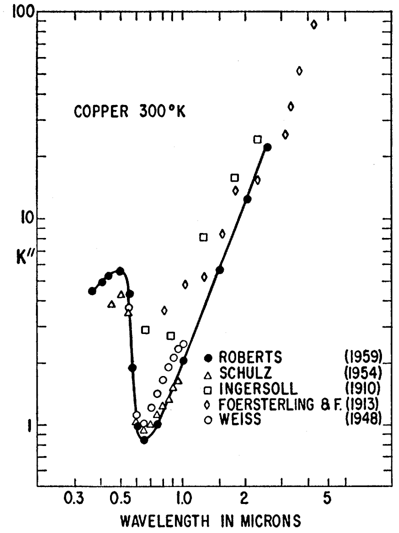

FIG. 4. Imaginary part of dielectric constant of copper at 300°K.

VI. INTERPRETATION OF OPTICAL DATA

The bound electrons are considered to be dominant in copper at wavelengths below 0.6 micron and account for the sudden change in K'' between 0.55 and 0.6 micron. Accordingly, one would expect to be able to expand the observed optical dielectric constant at wavelengths below 0.6 micron into a series of terms of the type indicated in the first summation in Eq. (6).

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[11] L. R. Ingersoll, Astrophys. J. **32**, 282 (1910).

[12] K. Foersterling and V. Freedericksz, Ann. Physik **40**, 201 (1913).

[13] K. Weiss, Z. Naturforsch. **3A**, 143 (1948).

[14] L. G. Schulz, J. Opt. Soc. Am. **44**, 357 (1954); L. G. Schulz and F. R. Tangherlini, J. Opt. Soc. Am. **44**, 362 (1954).

Such an expansion was actually carried out in the work on tungsten in paper II.[3] In the present case there does not seem to be enough detailed information on which to base such an expansion. If evaluated, the characteristic wavelengths λ_{sm} appearing in these terms would presumably correspond to electron transitions between specific energy states. The maximum value of λ_{sm} would, therefore, determine a minimum energy or threshold for interband transitions. In copper this would be about 2.1 ev. Since this threshold is very abrupt, it is evident that the bound electrons are quite ineffective in copper at wavelengths above 0.6 micron. Therefore the desired analysis of free electron terms can be made in the wavelength range 0.65 to 2.5 microns without the need to consider any bound electron terms in detail.

Equation (4) suggests that the real part of the dielectric constant, K', may be made up of two terms; a constant term and a term proportional to λ^2. To show that this is actually the case in the wavelength range 0.65 to 2.5 microns, K' is plotted versus λ^2 in Fig. 5. In this figure the experimental data do fall on straight lines at each temperature with very good precision except for points at the single wavelength of 2.5 microns. The deviation here of a few percent is believed to be due to the small amount of scattered light transmitted by the monochromator, an amount which is greatly accentuated at this wavelength.

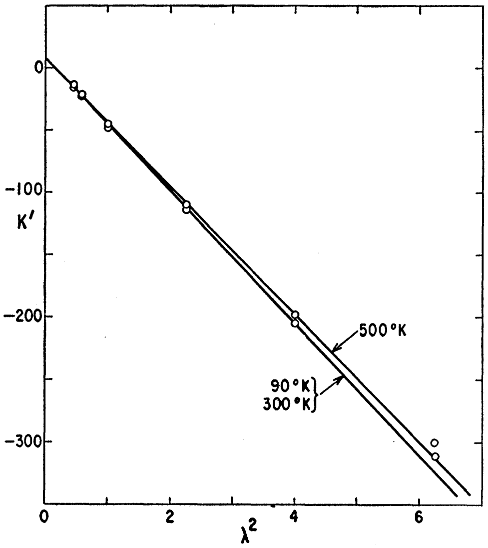

FIG. 5. K' versus square of wavelength in microns.

In Fig. 6 there is shown a plot of K''/λ versus λ^2. Here again the data fall precisely on straight lines with the single exception noted above. However, these straight lines do not pass through the origin, a fact which indicates that the expression for K'' includes a linear term in λ in addition to the cubic term which is anticipated according to Eq. (4). The observed dependence of K' and K'' on wavelength as indicated in Figs. 5 and 6 may be summed up in the following empirical formula.

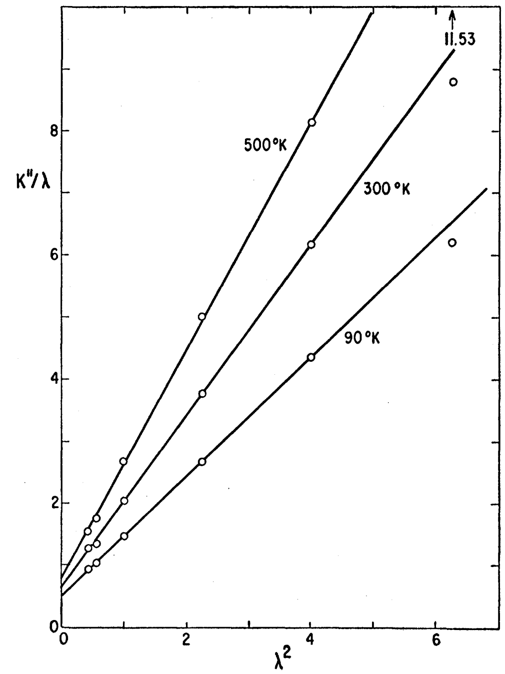

FIG. 6. K''/λ versus square of wavelength (λ) in microns.

$$K = A - B\lambda^2 - i(C\lambda + D\lambda^3). \qquad (8)$$

The values of the parameters A, B, C, and D determined from the slopes and intercepts of the straight lines in Figs. 5 and 6 are listed in Table III. Since for the most part A is rather small in comparison with $B\lambda^2$, one may neglect A in calculating the skin depth. If this is done, the skin depth is independent of wavelength and is equal to the calculated values shown in Table III. This table also shows values of the dc conductivity, σ_0, based on the work of Meissner,[15] Holborn,[16] and Pawlek and Reichel.[17]

If one sets aside the term in Eq. (8) containing C, then the remaining terms in this equation depend on wavelength in the same manner as corresponding terms in Eq. (4). It seems natural to try to assign

TABLE III. Experimentally determined parameters for copper.

	90°K	300°K	500°K
$A = K_\infty = 1 + \Sigma_m K_{0m}$	6	6	6
B	52.8	52.8	$51.2 \times 10^{12} m^{-2}$
C	0.50	0.65	$0.80 \times 10^6 m^{-1}$
D	0.97	1.38	$1.86 \times 10^{18} m^{-3}$
$\delta = \lambda / 2\pi\sqrt{-K'}$	0.0219	0.0219	$0.0222 \times 10^{-6} m$
σ_0	349	57.7	32.5×10^6 ohm$^{-1}m^{-1}$

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[15] W. Meissner, Ann. Physik **47**, 1001 (1915).
[16] L. Holborn, Ann. Physik **59**, 145 (1919).
[17] F. Pawlek and K. Reichel, Z. Metallk. **47**, 347 (1956).

TABLE IV. Proposed alternative parameters for copper.

	90°K	300°K	500°K
σ_1	346.5	55.2	30.0×10^6 ohm$^{-1}m^{-1}$
σ_2	2.5	2.5	2.5
σ_3	0.0083	0.0108	0.0133
λ_{r1}	470.6	76.3	$42.28\times10^{-6}m$
λ_{r2}	17.3	17.3	17.3
$l_1=\dfrac{\sigma_1}{1546\times10^{12}}$	0.2241	0.0357	$0.0194\times10^{-6}m$
$\alpha_1=1+\dfrac{3}{8}\dfrac{l_1}{\delta}$	4.837	1.611	1.328

values to the parameters in Eq. (4) so as to fit the experimental values of B and D as defined in Eq. (8). It is certainly possible to find values of λ_0 and α which satisfy this requirement at any one temperature. This may be done using the following relations.

$$\lambda_0=\sigma_0/2\pi c\epsilon_0 B;\quad \alpha=\lambda_0 D/B. \tag{9}$$

The question, then, is whether the values of λ_0 and α determined by Eq. (9) at different temperatures are mutually consistent and in accord with other data on mean free path.

The mean free path may be calculated from the known values of α and δ by use of Eq. (5). The ratios of σ_0/l obtained from values of mean free path calculated in this way are: 1432×10^{12} ohm$^{-1}m^{-2}$ at 500°K, 1387×10^{12} at 300°K, and 951×10^{12} at 90°K. The first two values seem in reasonably close agreement with the value $\sigma_0/l=1546\times10^{12}$ ohm$^{-1}m^{-2}$ obtained by Chambers and reported by Sondheimer.[18] This agreement tends to support the choice $p=0$, since any other value of p would give a less favorable comparison.

The results at 90°K, however, do not fit this interpretation at all, because it would seem absurd to suppose that σ_0/l would be so much different at the low temperature. There is no plausible variation of p with temperature that would lead to a more satisfactory interpretation, therefore it must be concluded that Eq. (4) is not sufficient by itself to account for the observed values of B and D at all temperatures.

The next logical step is to show that the particular form of Eq. (6) which includes two free-electron terms is at least sufficient to explain the observed values of B and D. As a matter of fact the extra term is more than sufficient, so there is a certain degree of arbitrariness in the procedure of choosing parameters to fit the experimental data. One possible interpretation, which also accounts for the term containing C, is that given below.

It appears that a close parallel can be drawn between copper and nickel, the latter having been already studied in detail in paper II.[3] In other words both metals have the same number of free electron terms expressed in the form of Eq. (6). One of these terms contains most of the dc conductivity and changes accordingly with temperature. The mean free path in copper determined by Chambers would naturally be expected to apply only to this one term. The other free electron terms have much shorter relaxation wavelengths and most likely the corresponding mean free paths would be very short compared with δ. These other terms are relatively independent of temperature.

In copper both λ_{r1} and λ_{r2}, corresponding to the two leading terms, seem to be much longer than any wavelength used in the experiments, so that extreme relaxation conditions prevail for both of these terms. These are the same terms which account for the values of B and D. The term involving C would be interpreted in the same way as in nickel by a third free electron term having a very short relaxation wavelength. A summary of the proposed values of the parameters is given in Table IV. The mean free paths shown in this table are wholly consistent with Chambers' observed value of σ_1/l_1. When these values are substituted in Eq. (6) and when this equation is modified in the manner of Eq. (4), then all the values of B, C, D, and σ_0 obtained at each temperature agree very closely with those listed in Table III. Table IV may be compared with Table I for nickel in paper II.[3]

Although there are certain formal similarities between optical properties of copper and nickel, there are also some important differences in the numbers involved. In copper the imaginary part of the term containing σ_1 is larger than that of the term containing σ_2 at each temperature. Since the term containing σ_1 varies with temperature and is modified further by the anomalous skin effect, both of these factors have a bearing on the optical properties of copper. In nickel the imaginary part of the term containing σ_1 is very much smaller than that of the term containing σ_2, as shown in Fig. 3 of paper II.[3] For this reason the reported optical properties of nickel are nearly independent of temperature and give no measurable evidence of the anomalous skin effect.

Since there is such excellent agreement with Eq. (8) in the range of wavelength above 0.6 μ covered in the author's experiments, it may be of interest to extrapolate these results to still longer wavelengths. The values

TABLE V. Calculated and observed optical constants of copper at 2.5 and 10 microns.

	2.5 μ		10 μ	
	K'	K''	K'	K''
Roberts (calculated from Eq. 8)				
Bare copper	−325	23.2	−5274	1386
Same with 40 A film	−243	19.0	−3988	902
Beattie and Conn[a] (experimental)				
Annealed and electropolished	−150	30	−1900	920
Buffed	−220	25	−2500	750
Shkliarevskii and Padalka[b]	−204	26.9	−3406	1248

[a] See reference 19.
[b] See reference 20.

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[18] E. H. Sondheimer, Suppl. Phil. Mag. 1, 1 (1952).

of K' and K'' at 2.5 μ and 10 μ obtained by means of Eq. (8) using the data compiled in Table III are shown after the heading "bare copper" in Table V. Note that the values of K' and K'' at 2.5 μ are about 5% greater in absolute value than the observed values given in Table II. The reason for this, as already pointed out, is that there is believed to be a slight error in the experimental values at this wavelength owing to scattered light transmitted by the monochromator.

Table V also shows data at 2.5 μ and 10 μ as reported by Beattie and Conn[19] and by Shkliarevskii and Padalka[20] or obtained from their data by interpolation. Evidently these authors have made measurements on copper exposed to the atmosphere under the assumption that their results would not be affected much by an oxide film that was extremely thin compared with the wavelength. In order to check this hypothesis the values have been calculated for the effective optical constants that would be measured on a copper surface covered with a dielectric layer of refractive index 2.5 and only 40 A thick. The results of this calculation are shown in Table V just underneath the author's values for bare copper. This calculation is carried out using the formulas summarized in Appendix II. One finds that the dielectric layer causes a very great difference even at the longer wavelength for which the film thickness is only 4×10^{-4} times the wavelength. Furthermore, the effect of the surface layer is about the right order of magnitude to explain the differences between the values calculated in the present work and the older experimental data. It is clear from this that just as much care needs to be exercised in obtaining a clean surface for measurements at long wavelengths as is needed at short wavelengths.

VII. CONCLUSIONS

The optical properties of copper, expressed in the form of a complex dielectric constant, $K'-iK''$, have been measured under conditions which approach as closely as possible to a clean, plane polycrystalline surface free of mechanical cold-working. The development of reasonably sized crystal grains free of cold-working was ensured first of all, by using specimens of solid metal; secondly, by thoroughly annealing the specimens in hydrogen; and thirdly, by electropolishing to produce the finished surface. Measurements confirmed that specimens so prepared did possess surface films, presumably of cuprous oxide. Finally, it was learned that the above specimens could be made clean by heating them to 227°C in a vacuum amounting to an absolute pressure of about 10^{-5} mm (Hg). This was a sufficiently good vacuum to maintain the surfaces clean enough for the required measurements. Refinements in the measuring apparatus and technique permitted highly reliable observations throughout most of the range from 0.365 to 2.5 microns. Complete sets of data were obtained and are reported at 90°, 300°, and 500°K.

In the wavelength range below 0.6 micron the author's data confirm the known facts relating to a threshold for interband electronic transitions in copper. At longer wavelengths the observed values of K' and K'' may be expressed in powers of λ. However, the resulting expression is not quite what one would expect in a metal having free electrons with a single relaxation time and, consequently, a spherical Fermi surface. The imaginary part of the dielectric constant, K'', does have a term proportional to the cube of λ, which would be expected on the basis of a single relaxation time, but it also has a term which is linear in λ and which cannot be explained in this way. Furthermore, the coefficient of the cubic term is too large to be consistent with the other data and with the known values of mean free path. This is especially important at 90°K. All these inconsistencies may be resolved if it is assumed that the free electrons in copper have not one but several discrete relaxation times. The same is true for other metals which the author has considered previously.

The complication involving several relaxation times instead of one is thought to be a consequence of the fact that in copper the Fermi surface is not spherical. Pippard[21] and Cohen[22] have recently shown evidence that the Fermi surface of copper is not only nonspherical, but that it even touches the Brillouin zone boundary. Pippard's work was based on the study of the anomalous skin effect in oriented crystals at microwave frequencies. Cohen's treatment was based on a comparison of the thermal effective mass with the optical mass, the latter being derived from just the real part of the dielectric constant. The author's work may therefore be regarded not only as a quantitative model for the observed relaxation effects in optical properties but also as independent support for what is already known about the nonsphericity of the Fermi surface of copper.

VIII. ACKNOWLEDGMENTS

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APPENDIX I

The relative intensities of the transmitted radiation corresponding to different combined settings of the two main polarizers, P_1 and P_2, were worked out by Beattie[23] under the assumption that unpolarized radiation was incident on P_1. His Eqs. (2), (3), and (5) are assembled here as Eq. (10) with a change in sign

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[19] J. R. Beattie and G. K. T. Conn, Phil. Mag. **46**, 989 (1955).

[20] I. N. Shkliarevskii and V. G. Padalka, Optika i Spektroskopiya **6**, 78 (1959).

[21] A. B. Pippard, Phil. Trans. Roy. Soc. (London) **A250**, 325 (1957).

[22] M. H. Cohen, Phil. Mag. **3**, 762 (1958).

[23] J. R. Beattie, Phil. Mag. **46**, 235 (1955).

of angular notation. The need for the change arises because the author's prisms are arranged symmetrically around the vacuum chamber so that the rotation of one scale is reversed relative to the direction of the light path. The I_0 is a constant related to the incident intensity.

$$I_1=\tfrac{1}{2}I_0; \qquad (P_1=\pi/2;\quad P_2=\pm\pi/4)$$

$$I_2=\tfrac{1}{2}\rho^2 I_0; \qquad (P_1=0;\quad P_2=\pm\pi/4)$$

$$I_3=\frac{I_0}{4}(1+\rho^2+2\rho\cos\Delta); \; (P_1=\mp\pi/4;\; P_2=\pm\pi/4) \quad (10)$$

$$I_4=\frac{I_0}{4}(1+\rho^2-2\rho\cos\Delta); \; (P_1=\pm\pi/4;\; P_2=\pm\pi/4).$$

The intensity ratios measured by the author may be defined in the following way:

$$e_s=\tfrac{1}{2}(I_4/I_1);\quad \sigma_s=\tfrac{1}{2}(I_3/I_1);$$
$$e_p=\tfrac{1}{2}(I_4/I_2);\quad \sigma_p=\tfrac{1}{2}(I_3/I_2). \quad (11)$$

The additional factor of $\frac{1}{2}$ in each case comes from the loss introduced by the third prism, P_3. For example, suppose the settings are $P_1=\pi/2$, $P_2=\pi/4$, and $P_3=\pi/2$. According to the above table the indicated intensity would be a measure of I_1. Now, suppose P_1 alone is shifted to $\pi/4$. Then P_1 will transmit only half of the light from P_3 and the indicated intensity would be a measure of $I_4/2$. The ratio of these two transmitted intensity readings would be equal to e_s as it is defined above. The above expressions lead to the following formulas for $\tan\psi$ and $\cos\Delta$.

$$\rho^4=\tan^4\psi=\sigma_s e_s/\sigma_p e_p,\quad \cos^2\Delta=(\sigma_s-e_s)(\sigma_p-e_p). \quad (12)$$

The self-consistency of the observed intensity ratios may be checked by testing them in the following identities

$$\sigma_s e_p/\sigma_p e_s=1, \quad (13)$$

$$\frac{(e_p-1/2)(e_s-1/2)}{(\sigma_p-1/2)(\sigma_s-1/2)}=1. \quad (14)$$

APPENDIX II

The treatment of the surface film is simplified by the assumption that the film is homogeneous and isotropic and of constant thickness, d. In the following expressions the subscript 1 is used in reference to the vacuum, the subscript 2 is used to refer to the metal, and the subscript 3 is used for the surface film. By this convention K_1 is unity, K_2 is the complex dielectric constant of the metal, and K_3 is the dielectric constant of the film. In the numerical calculations real numbers are substituted for K_3, but the equations are equally valid for an absorbing film in which K_3 would be complex. The subscripts s and p refer, respectively, to polarization perpendicular to the plane of incidence and parallel to it.

Instead of writing a single expression for the final result it is preferred to approach the solution in a series of stages involving the following definitions. Let

$$n_{sm}=(K_m-\sin^2\phi_1)^{\frac{1}{2}}/\cos\phi_1,$$
$$n_{pm}=K_m/n_{sm};\quad (m=2 \text{ or } 3). \quad (15)$$

And let:

$$r=i\tan(2\pi d n_{s3}\cos\phi_1/\lambda). \quad (16)$$

Then let:

$$n_v=\frac{n_{v3}(n_{v2}+rn_{v3})}{n_{v3}+rn_{v2}};\quad (v=s \text{ or } p). \quad (17)$$

Finally:

$$\tan\psi e^{i\Delta}=\frac{(n_s+1)(1-n_p)}{(n_s-1)(1+n_p)}. \quad (18)$$

The values of ψ and Δ obtained in this way may be used in the calculation of an effective dielectric constant by substituting in Eq. (7). If there were no surface film ($d=0$), the result of this calculation would simply be K_2. The author has attempted to obtain surfaces with a sufficiently thin film so that there will be no significant difference between K_2 and the value of K determined by Eq. (7). The above equations, (15) through (18), give a means for estimating how thin such a film has to be. They also give a means for estimating how large the error will be if measurements are made on a surface having a film even though the dielectric constant is calculated as if there were no film.

One step in the series of calculations may be dropped if Eq. (18) is substituted in Eq. (7) so as to eliminate ψ and Δ.

$$K_{\text{eff}}=\sin^2\phi_1\left[1+\tan^2\phi_1\left(\frac{n_s n_p-1}{n_s-n_p}\right)^2\right]. \quad (19)$$

It might be thought that a further simplification could be accomplished by eliminating other steps in the process and that one could finally solve for K_2 in terms of K_{eff}, K_3, and d. Attempts to do this have been disappointing. Various approximate solutions have been proposed but it is difficult to keep track of whether the approximations are valid in a given situation and the approximate solutions are so complicated anyway that it is hardly any more difficult to run through the exact equations (15), (16), (17), and (19).