

## Optical Absorption of Copper and Silver at 4.2°K

MANFRED A. BIONDI

*Westinghouse Research Laboratories, Pittsburgh, Pennsylvania*

(Received February 8, 1956)

Measurements of the optical absorption of copper and silver are made over the wavelength range 0.3–3.3 $\mu$  at a temperature of 4.2°K where the classical mean free path of the conduction electrons is much greater than the depth of penetration of the electromagnetic field. The absorptivity is determined calorimetrically, i.e., from the temperature rise produced in the sample by the absorption of the incident radiation. In the infrared ( $\lambda > 1.5\mu$ ) the absorptivity,  $A$ , is found to be independent of wavelength. The measured values,  $A = 0.0050$  for copper and  $A = 0.0044$  for silver, are in good agreement with the values obtained from theory. These results suggest that the infrared absorptivity results from absorption of photons by conduction electrons (a) during diffuse internal reflection of the electrons from the surface of the metal and (b) during phonon-generating collisions in the skin-depth layer.

ACCORDING to the classical Drude-Lorentz theory<sup>1</sup> the interaction of the conduction electrons of a metal with electromagnetic radiation incident normally on the metallic surface leads to an absorptivity

$$A_{cl} = (m^*/\pi n e^2)^{1/2} (v_0/l), \quad (1)$$

where  $m^*$ ,  $n$ ,  $e$ , and  $l$  are the effective mass, density, charge, and mean free path, respectively, of the conduction electrons and  $v_0$  is the Fermi velocity. This theory, which is valid so long as the electron mean free path,  $l$ , is small compared to  $\delta$ , the skin depth of penetration of the field, predicts that the absorption should decrease without limit as  $l$  increases. However, experimental measurements reveal that the absorptivity of metals at liquid helium temperatures is the same order of magnitude as at room temperature, even though  $l$  has increased by orders of magnitude over its room temperature value. This effect, which has been called "the anomalous skin effect," results from the circumstance that  $l \geq \delta$ , and consequently the classical theory is not valid. The quantitative theory of the anomalous skin effect was developed formally by Reuter and Sondheimer<sup>2</sup> for the cases of diffuse and specular internal reflection of electrons at the surface of the metal. Using energy balance considerations, Holstein<sup>3</sup> derived simple formulas for the absorptivity of metals in the optical region which agreed with Reuter and Sondheimer's specular reflection results but gave a larger value of absorptivity for the case of diffuse reflection. Subsequently, Dingle<sup>4</sup> simplified Reuter and Sondheimer's formal expressions and obtained expressions in agreement with those of Holstein.

The only available experimental measurements in the optical region were those of Ramanathan,<sup>5</sup> who had measured the absorptivity of copper for room temperature radiation ( $\lambda \sim 14\mu$ ) and obtained a value  $A = 0.0062$ . This result is in order of magnitude agreement with the

theoretically predicted value  $A \approx 0.003$ . In order to investigate the problem in greater detail, the present experiment was devised to measure the absorptivity of metals as a function of wavelength over the visible and near-infrared regions.

### I. EXPERIMENTAL APPARATUS

The basis of the absorption measurements is calorimetric, i.e., the energy absorbed on the surface of a metal sample is determined from the rise in temperature of the specimen. A schematic diagram of the apparatus is given in Fig. 1. Part (a) illustrates the over-all apparatus while part (b) represents an enlarged view of the measuring section which is immersed in liquid helium.

The source of radiation is a 1000-watt incandescent tungsten projection lamp. The desired wavelength is obtained either by the use of filters or by means of a Gaertner infrared monochromator. The light is transmitted through an optical system consisting of four quartz lenses and focused on the polished surface of the target at an angle of incidence of 15°. The radiation is then reflected onto a gold black absorbing surface,<sup>6</sup> whose absorptivity is greater than 99% over the wavelength range of the present experiment.

The target and the black absorber are threaded into stages made of copper; imbedded in each stage is a carbon resistance thermometer<sup>7</sup> and a heater winding consisting of 100 ohms of manganin resistance wire. Each stage is supported by thin-walled stainless steel tubing which is connected to the base. Heat leaks between the stages and the base take the form of copper wires of the proper conductance to give thermal time constants of  $\sim 10$  seconds for each stage. Stray radiation which might get by the target is prevented from reaching highly absorbing surfaces on the target stage by a blackened stop which is attached to the base. The base also contains a resistance thermometer. The electrical

<sup>1</sup> See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1936 and 1953).

<sup>2</sup> G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1948).

<sup>3</sup> T. Holstein, Phys. Rev. **88**, 1425 (1952).

<sup>4</sup> R. B. Dingle, Physica **19**, 311 (1953).

<sup>5</sup> K. G. Ramanathan, Proc. Soc. (London) **A65**, 532 (1952).

<sup>6</sup> See, for example, L. Harris *et al.*, J. Opt. Soc. Am. **38**, 582 (1948). The author is indebted to M. Garbuny for the preparation of the gold black surfaces.

<sup>7</sup> Allen-Bradley Company, Milwaukee, Wisconsin, 56-ohm,  $\frac{1}{2}$ -watt carbon resistor.

leads from the various heaters and thermometers are of 0.003-inch diameter niobium wire to minimize heat generation and thermal conduction in the leads. The electrical leads are connected to an 18-lead Kovar-glass vacuum-tight plug which is attached to the base plate. The vacuum seal between the measuring section and the outer envelope of the apparatus is made by means of a gold O-ring clamped between beryllium-copper flanges. The apparatus is evacuated by means of an oil diffusion pumping system in order to prevent significant gas conduction between the stages. The values of the various resistance thermometers and of the dc power in the heaters are measured by means of a precision potentiometer.

## II. EXPERIMENTAL OPERATION

In order to determine the absorptivity of the target for a particular wavelength, the appropriate filter (see the transmission curves of Fig. 2) is used with the incandescent source running at a temperature which gives between  $10^{-4}$  and  $10^{-9}$  watt of power incident on the target. After steady state is reached the values of the resistance thermometers in the target and the absorber stages and in the base are measured. It is found that, in addition to the substantial rises in temperature of the target and the absorber stages ( $\sim 0.01^\circ\text{K}$ ), the base temperature rises slightly above the bath temperature ( $\sim 0.001^\circ\text{K}$ ) as a result of the noninfinite thermal conductivity of the liquid helium in contact with the base plate. With the source turned off, the values of each of the three thermometers are again measured. Power is then applied to the target heater to reproduce the temperature difference obtained with the source on. In similar fashion, power is applied to the absorber stage heater to reproduce its temperature rise. The power in each stage is measured. Then, with both

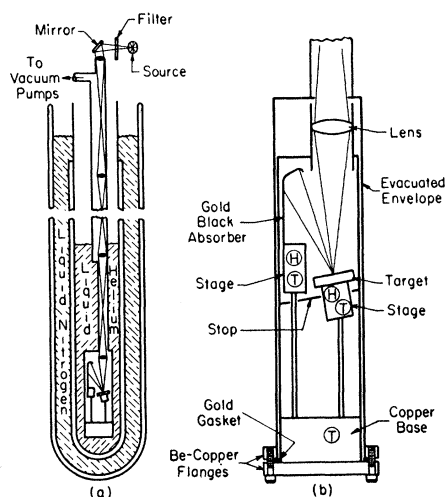


FIG. 1. (a) Schematic diagram of the over-all apparatus. (b) Enlarged view of the measuring section, which is immersed in the liquid helium bath. The symbols  $H$  and  $T$  refer to dc heaters and carbon resistance thermometers, respectively.

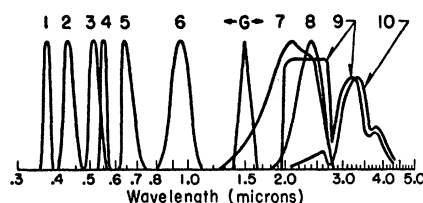


FIG. 2. Relative transmission curves of the various filter systems used with the incandescent source. Numbers 1-8 are Corning glass narrow band-pass filters, number 9 consists of a germanium filter together with the quartz optics of the apparatus, and number 10 results from the quartz optics' transmission of energy from the source running at  $780^\circ\text{K}$ . The curve  $G$  represents the band transmitted by a Gaertner infrared monochromator which transmits sufficient energy from the source for measurements over the range 1.2 to  $2.0\mu$ .

heaters turned off, the value of the base resistance thermometer is once again measured to be certain that the bath temperature did not drift in the course of the measurements. Using this procedure, one obtains data which are reproducible to within two percent.

## III. MEASUREMENTS

The measurements of the absorptivity of copper and of silver are shown in Figs. 3 and 4. The preparation of the samples of high purity copper and silver is described in detail in the appendix. The radiation from the source (unpolarized) is incident on the target at an angle of  $15^\circ$  from the normal; therefore the data of Figs. 3 and 4 are multiplied by the factor 1.033 to obtain the absorptivity at normal incidence.<sup>8</sup> Figure 3 exhibits the band absorption found at the shorter wavelengths in copper and silver. The filters used (see Fig. 2) are not sufficiently sharp in wavelength selection to give the accurate shape of the absorption bands, but the curves are in agreement with the general picture of broad absorption bands at  $0.45\mu$  in copper and at  $0.27\mu$  in silver.<sup>9</sup> It is interesting to note that in Fig. 4, which shows the data on an expanded absorptivity scale, it is clear that the absorption bands do not disappear at  $0.5$ - $0.6\mu$  but extend weakly to  $\sim 1.5\mu$ . In many of the previous studies<sup>9</sup> this behavior was masked by substantial long wave absorption in the imperfect surface layer produced by mechanical polishing. The "tailing" of the absorption bands found in the present work may result from the contribution of "indirect" electronic transitions ( $\mathbf{k}_{\text{final}} \neq \mathbf{k}_{\text{initial}}$ ) involving phonon generation<sup>10</sup>; however, in view of the complicated structure of the conduction bands of copper and silver,<sup>1</sup> other explanations are possible.

At long wavelengths ( $> 1.5\mu$ ) the absorptivity becomes independent of wavelength; the normal incidence

<sup>8</sup> This correction is obtained by calculating the average decrease in the field inside the metal as a result of the oblique incidence of the unpolarized light. For small angles,  $\theta$ , from the normal the correction is  $1 + \frac{1}{2}\theta^2$ .

<sup>9</sup> See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 655.

<sup>10</sup> This process has been suggested for germanium; see Hall, Bardeen, and Blatt, *Phys. Rev.* **95**, 559 (1954).

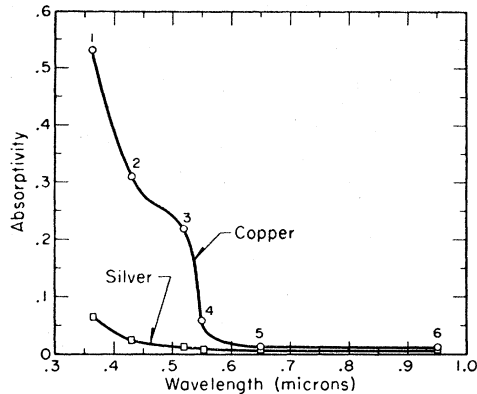


FIG. 3. Absorptivity versus wavelength of polycrystalline samples of copper and silver at 4.2°K and at an angle of incidence of 15° from the normal.

value for copper is 0.0050 and for silver is 0.0044. The value for copper differs by 20% from the value reported in an earlier paper<sup>11</sup>; however, elimination of an error in the earlier measurement procedure leads to good agreement (within 4%) with the present results.

We attribute the infrared absorptivity of silver and copper to the interaction of the "free" conduction electrons with photons in the skin-depth layer near the surface of the metal. The experimental results are compared with theoretical predictions in Sec. V.

#### IV. THEORY

The theory for the "anomalous skin effect," i.e., the absorption of electromagnetic energy by conduction electrons for the case that  $l > \delta$ , has been developed by a number of investigators.<sup>2-4</sup> In these formulations, which treat the electromagnetic radiation classically, the optical (high frequency) absorption is the result of the motion of conduction electrons from the interior into the skin-depth region near the surface of the metal, where they acquire an oscillatory energy from the field. The electrons then make a collision with the surface of the metal and are "reflected" either specularly or diffusely back into the interior of the metal. As a result of the surface collision a part or all of the oscillatory energy is converted to random or thermal energy of the electron which is later imparted to the lattice in the interior of the metal.

For the optical region, Holstein has obtained a very simple expression for the absorptivity,  $A$ , in terms of the fraction  $p$  of electrons which are specularly reflected,  $(1-p)$  being diffusely reflected<sup>5</sup>:

$$A_{\text{an}} = p \left( \frac{2\pi n e^2}{m^* \omega^2} \right) \frac{v_0^3}{c^3} + (1-p) \frac{v_0}{4c}, \quad (2)$$

<sup>11</sup> M. A. Biondi, Phys. Rev. **96**, 534 (1954). In this earlier work the data were improperly corrected for the effect of leakage radiation striking the back surfaces of the target stage. When this correction was redetermined, using improved measuring methods, a value  $A = 0.0048$  was obtained for copper. In the present apparatus the correction for leakage radiation is small (<2%) as a result of the effective stop placed just behind the target surface.

where  $\omega$  is the radian frequency and  $c$  the velocity of light. If one substitutes numbers into Eq. (2), one finds that in the optical region, unless  $p$  is very nearly unity, the second term (diffuse reflection) is much larger than the first term. In practice, it is found that in the radio-frequency,<sup>12</sup> microwave,<sup>13</sup> and optical regions the best agreement with theory is obtained for completely diffuse ( $p=0$ ) reflection.

It has been shown<sup>14</sup> that an identical result for the optical absorptivity is obtained when the problem is formulated quantum mechanically. From this standpoint, the "free" conduction electrons are unable to absorb a light quantum directly because of the requirement of momentum and energy conservation. It is necessary that the electron make a scattering collision (provided by the diffuse reflection at the surface) to satisfy conservation conditions.

One can obtain an approximate expression<sup>15</sup> for the anomalous skin-effect absorptivity from the usual classical formula [Eq. (1)] for the diffuse reflection case by noting that each transit of the electron through the skin depth region results in *one* scattering collision (at the surface). Thus, the mean free path for scattering in the classical formula is replaced by

$$l \simeq 2\delta = 2(m^*c^2/4\pi ne^2)^{1/2}. \quad (3)$$

Substituting this value of  $l$  into Eq. (1), one obtains

$$A_{\text{an}} \simeq v_0/c \quad (4)$$

for the anomalous absorptivity, which differs only by the numerical factor  $\frac{3}{4}$  from the exact expression, Eq. (2).

The experimental work of Ramanathan yielded a value for the absorptivity of copper ( $A = 0.0062$ ) which was in order-of-magnitude agreement with the predictions of the theory of the anomalous skin effect ( $A = 0.0029$ ).<sup>16</sup> However, in the present work we obtain

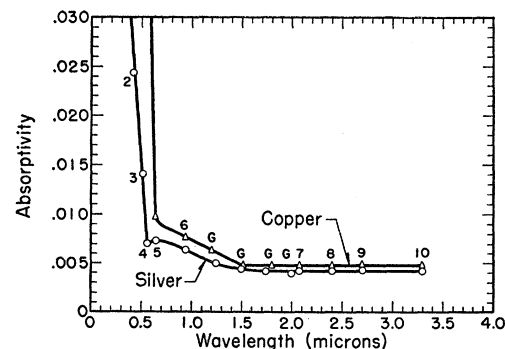


FIG. 4. Absorptivity versus wavelengths of polycrystalline samples of copper and silver at 4.2°K and a 15° angle of incidence.

<sup>12</sup> M. P. Garfunkel and L. J. Varnerin. Phys. Rev. **99**, 1647(A) (1955).

<sup>13</sup> R. G. Chambers, Proc. Roy. Soc. (London) **A215**, 481 (1952).

<sup>14</sup> R. Wolfe, Proc. Phys. Soc. (London) **A68**, 121 (1955).

<sup>15</sup> T. Holstein, Phys. Rev. **99**, 1647(T) (1955).

<sup>16</sup> See discussion in Sec. V.

a value  $A = 0.0050$  which, while in better agreement with theory, still exhibits a discrepancy well outside of expected experimental and theoretical errors. This result has led to a re-examination<sup>17</sup> of the problem of optical absorption under conditions in which the "classical" mean free path for electron scattering is much larger than the skin depth. At low temperatures, the lattice is in zero-point vibration and thus the phonons, which contribute strongly to electron scattering at ordinary temperatures, are absent. However, there is still the process in which an electron in the skin-depth region absorbs a photon and then interacts with the lattice to generate a phonon to permit conservation of energy and momentum. It is found that the mean free path for such a process is comparable to the skin depth. This "volume collision" (as opposed to the surface collision of the anomalous skin effect) absorption is given<sup>17</sup> by a formula identical to the classical form of Eq. (1), i.e.,

$$A_v = (m^*/\pi n e^2)^{1/2} (1/\tau_{\text{eff}}) \quad (5)$$

except that the usual conductivity relaxation time,  $\tau$ , is replaced by an effective time,  $\tau_{\text{eff}}$ , given by

$$\tau_{\text{eff}} = 5/2(T\tau/\Theta),$$

where  $\tau$  is the conductivity relaxation time at a temperature  $T$ , large compared to the Debye  $\Theta$ . Thus the total absorptivity of a metal is equal to the sum of the contributions from surface scattering of the electrons, Eq. (2), and scattering in the skin-depth volume, Eq. (5).

## V. DISCUSSION

The measurements given in Figs. 3 and 4 refer to polycrystalline samples of copper and silver. In earlier studies of copper<sup>11</sup> no difference in absorptivity was found between polycrystalline and single crystal samples. The measured values for copper and silver at long wavelengths ( $\lambda > 1.5\mu$ ) are compared with the theoretical values calculated using Eqs. (2) and (5) in Table I. The values used in these equations are, for copper and silver, respectively:  $m^*/m = 1.38$  and  $0.96$ ,<sup>18</sup>  $n_e = 8.5 \times 10^{22}$  and  $5.9 \times 10^{22}$  per cc,<sup>1</sup>  $\Theta = 344$  and  $225^\circ\text{K}$ ,<sup>18</sup> and  $T\tau = 1.0 \times 10^{-11}$  and  $1.5 \times 10^{-11}$  °K-sec.<sup>1,13</sup> Copper and silver were chosen because of the greatly differing surface and volume contributions to their absorptivities.

The agreement between theory and experiment concerning the absolute magnitude of the absorptivities is within the combined uncertainties of the theoretical calculation and the experimental measurements. In addition, the observed lack of dependence of absorptivity on wavelength over the range  $1.5$ – $3.3\mu$  is in accordance with the theoretical prediction that both surface and volume absorption by the conduction electrons are

TABLE I. Comparison of the theoretical and experimental values of absorptivity.

Metal	Surface	Theory Volume	Total	Experiment
Copper	0.0029	0.0020	0.0049	0.0050
Silver	0.0036	0.0009	0.0045	0.0044

not frequency dependent. Finally, over the extremely limited temperature range attainable with the present apparatus,  $4.2$ – $3.4^\circ\text{K}$ , the absorptivity is found to be independent of temperature, in agreement with theory. These results lead us to conclude that at low temperatures and at optical frequencies the significant processes which lead to the absorption of photons by conduction electrons involve diffuse scattering of the electrons from the surface of the metal and phonon generating collisions in the skin-depth volume.

## ACKNOWLEDGMENTS

The author wishes to thank the members of the Low Temperature Group, in particular A. Wexler, for their great assistance during the design of the apparatus. The author is indebted to T. Holstein for many valuable discussions concerning the theoretical aspects of the problem.

## APPENDIX. PREPARATION OF THE COPPER AND SILVER SAMPLES

The copper targets were fabricated from high-purity (99.999+%) copper from the American Smelting and Refining Company and from a sample of commercial OFHC copper which was found to have a low impurity content. The silver samples were 99.98% pure material supplied by the Handy and Harmon Company. The impurity content in these specimens was sufficiently small so that the electron mean free path at  $4^\circ\text{K}$ , determined from resistance measurements, was  $\sim 10^{-3}$  cm, more than 100 times greater than the electromagnetic skin depth ( $\sim 2 \times 10^{-6}$  cm) at optical frequencies. The copper targets were machined from single-crystal and polycrystalline zone-melted stock. The silver targets were machined from vacuum melted ingots. The copper and silver targets were faced with a diamond cutting tool, mechanically polished with metallographic polishing paper, and electropolished to remove abrasives in the surface layer. They were then annealed for  $\sim 10$  hours either in vacuum or in a hydrogen atmosphere at  $\sim 30^\circ\text{C}$  below their melting points. They were then electropolished, multiply rinsed in absolute alcohol and boiled distilled water, and mounted in the apparatus under a helium atmosphere to prevent oxidation. Before mounting, the target surface was examined under magnification for flaws or surface films by the use of grazing incidence illumination. It was found that targets with a noticeable film on them consistently gave slightly higher ( $\sim 10\%$ ) values of absorptivity.

<sup>17</sup> T. Holstein, *Phys. Rev.* **96**, 535 (1954).

<sup>18</sup> W. S. Corak *et al.*, *Phys. Rev.* **98**, 1699 (1955).