

The measured absorptivity of copper is shown in Fig. 2. Two samples of high-purity copper were used, one a single crystal, the other polycrystalline (crystal size  $\sim 2$  mm). The electronic mean free path of these samples at 4.2°K, determined from dc conductivity measurements, was  $l_e \geq 10^{-3}$  cm, which greatly exceeds the skin depth ( $\sim 2 \times 10^{-6}$  cm). The single-crystal target was vacuum annealed at 1040°C for 45 hours and electropolished. The polycrystal target was hydrogen annealed at 1020°C for six hours and then electropolished. The close agreement between the absorptivities of the two samples suggests that the measured values represent an intrinsic property of the copper rather than of the surface preparation. Over the range  $\lambda = 2.1 \mu - 4 \mu$ , we find  $A = 0.0039$ , independent of  $\lambda$ . The rapid rise in absorptivity at  $\lambda \leq 0.55 \mu$  is ascribed to direct interzonal transitions within the conduction band.<sup>7</sup> The long tail from  $\lambda = 0.55 \mu$  to  $2 \mu$  is either a continuation of this process or may possibly be caused by "indirect" electronic transitions ( $\mathbf{k}_{\text{final}} \neq \mathbf{k}_{\text{initial}}$ ) of the type recently predicted for germanium.<sup>8</sup>

In the present note, we shall discuss in detail only the absorption caused by the "free" electrons near the Fermi level and, therefore, shall consider only data for  $\lambda > 2 \mu$ . The observed lack of dependence of  $A$  on  $\lambda$  suggests that the electrons are diffusely reflected at the surface. Assuming one conduction electron per atom and  $m^* = m$ , where  $m$  is the free electron mass, Dingle<sup>3</sup> calculates  $A = 0.004$  ( $p = 0$ ), in excellent agreement with our observations. However, the assumption that  $m^* = m$  for electrons at the Fermi level is open to question. Specific heat measurements, which apply to these electrons, give  $m^* = 1.4m$  for copper. With this value of  $m^*$ , Eq. (1) gives  $A = 0.0028$  ( $p = 0$ ). The observed value is therefore too high if electrons can only make collisions at the surface of the metal. Holstein<sup>9</sup> has recently investigated the two-stage volume process in which a conduction electron absorbs a photon with

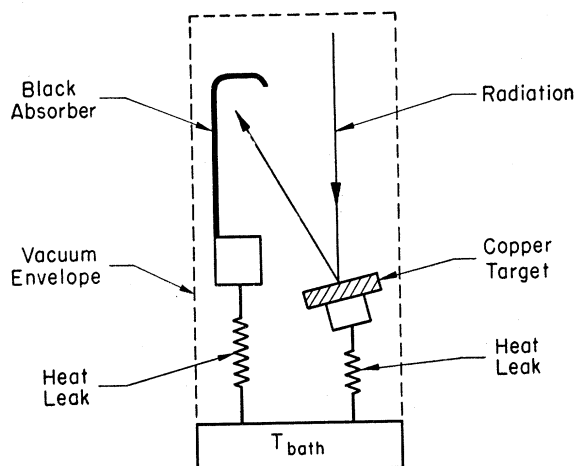


FIG. 1. Schematic diagram of the apparatus. The target and absorber stages each carry a resistance thermometer and a heater winding.

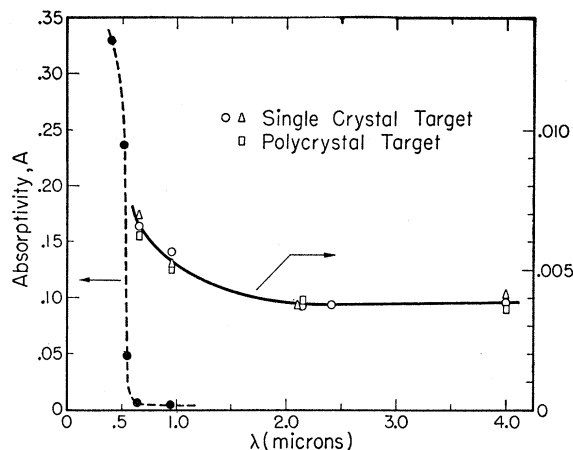


FIG. 2. Absorptivity of copper measured at 15° angle of incidence. Runs taken on the single crystal target on successive days are indicated by the symbols  $\circ$  and  $\Delta$ . The "free" electron absorption ( $\lambda > 2 \mu$ ) is 0.0039 (corrected to normal incidence). The scale for the solid curve is at the right of the figure, that for the dashed curve at the left.

simultaneous emission of a phonon. At optical and near infrared frequencies, the mean free path for this process is comparable to the skin depth; hence the absorptivity given by Eq. (1) is increased to 0.0046.<sup>9</sup>

The present experimental results are therefore in fair agreement with the predictions of theory for diffuse electron reflection. In view of the operation of the two-stage volume process in addition to the surface scattering of electrons, the measurements are being extended to other metals (e.g., silver) to provide more adequate tests of the various theories.

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<sup>1</sup> G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 33 (1948).

<sup>2</sup> T. Holstein, Phys. Rev. **88**, 1427 (1952).

<sup>3</sup> R. B. Dingle, Physica **19**, 311, 348 (1953).

<sup>4</sup> See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1936), Chap. V.

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

<sup>6</sup> The measured absorptivity of the gold black is  $A > 0.99$ .

<sup>7</sup> N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936).

<sup>8</sup> Hall, Bardeen, and Blatt, Phys. Rev. **95**, 559 (1954).

<sup>9</sup> T. Holstein, following Letter [Phys. Rev. **96**, 535 (1954)].

## Optical and Infrared Volume Absorptivity of Metals

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THIS letter gives the results of a quantum-mechanical treatment of the electromagnetic absorptivity of metallic conduction electrons in the optical

and near infrared frequency region. According to the formalism of second-order perturbation theory, the process is a two-stage one, involving the simultaneous absorption (or emission) of electromagnetic energy and the absorption (or emission) of lattice quanta. For each of these four possibilities, one calculates the transition probability between one-electron states of wave numbers  $\mathbf{k}$  and  $\mathbf{k}'$ . With the aid of these transition probabilities one computes the rate of energy transfer from the electromagnetic field to the material system (electrons plus phonons); the latter quantity leads directly to the absorptivity.

Close correspondence with the classical Drude-Lorentz theory is to be expected for sufficiently small  $\hbar\omega$  (specifically  $\hbar\omega \ll kT$ ); this expectation has been confirmed by detailed calculations. On the other hand, at sufficiently low temperatures such that  $T \ll \Theta$  (the Debye temperature), and for optical and infrared frequencies, where the two conditions  $\hbar\omega \gg k\Theta$ ,  $\hbar\omega \gg kT$  are fulfilled, radical deviations from the classical theory are encountered. The origin of these deviations may be described as follows.

According to the classical theory, the absorption is proportional to the rate of momentum-transfer from electrons to lattice vibrations. At low temperatures ( $T \ll \Theta$ ) this process is severely inhibited by the requirements of energy conservation. In particular, the energy available for the generation of an individual phonon is  $\sim kT$ . Hence, only the low-frequency, i.e., low-momentum, phonons can be emitted.<sup>1</sup>

In this connection, the chief significance of the quantum-mechanical treatment is that, in the two-stage process described above, a quantum of electromagnetic energy  $\hbar\omega$  is imparted to the electron, with the result that the energy available for the generation of a phonon is no longer  $kT$  but  $\hbar\omega \gg kT$ . If, in addition  $\hbar\omega \gg k\Theta$  as assumed in the treatment, phonons of all frequencies, and, hence, all possible momenta may be generated. It then follows that the momentum-transfer, and, hence, the absorptivity is much larger than that given by the Drude-Lorentz theory.

The specific result obtained for the absorptivity may be written in the form

$$A_v = \left( \frac{m^*}{4\pi n e^2} \right)^{\frac{1}{2}} \frac{2}{\tau_{\text{eff}}}, \quad (1)$$

where  $n$  and  $m^*$  are electron density and effective mass. In the case of the classical theory,  $\tau_{\text{eff}}$  would be the ordinary conductivity-relaxation time; in the quantum-mechanical case, however,  $\tau_{\text{eff}}$  is given by the formula,

$$1/\tau_{\text{eff}} = \frac{2}{5} (\Theta/T\tau), \quad (2)$$

where  $\tau$  is the value of the conductivity-relaxation time at some reference temperature  $T$ , large compared to the Debye  $\Theta$ .

The connection between  $\tau_{\text{eff}}$  and the high-temperature relaxation time may be explained as follows. As stated

above, the scattering responsible for  $\tau_{\text{eff}}$  involves the emission of the whole phonon spectrum. In this respect it is quite similar to the high temperature relaxation process. In fact, the principal difference between the two is that, in the case of  $\tau_{\text{eff}}$ , the zero-point lattice vibrations are alone active whereas, at high temperatures, the thermally excited vibrations are the primary scattering agents. Now, the intensity ratio of the two types of excitation is, apart from numerical factors,  $\Theta/T$ ; hence, the occurrence of the latter factor in (2).

It is of interest to compare (1) with the absorptivity

$$A_s = \frac{3}{4} v_0/c \quad (3)$$

arising from the anomalous skin effect.<sup>2</sup> One has

$$\frac{A_v}{A_s} = \frac{16}{15} \frac{\Theta}{T} \frac{\delta_f}{v_0},$$

where  $\delta_f = (m^*c^2/4\pi n e^2)^{\frac{1}{2}}$  is the high-frequency skin depth. In the case of copper, for example, with  $\Theta = 310^\circ\text{K}$ ,  $m^* = 1.4m$  (specific heat data),  $n = \text{atomic density} = 8.5 \times 10^{22} \text{ cm}^{-3}$ , room temperature ( $293^\circ\text{K}$ ) conductivity  $\sigma = 5.92 \times 10^5 \text{ ohm}^{-1} \text{ cm}^{-1}$ ,  $\sigma/v_0\tau = 1.54 \times 10^{11} \text{ ohm}^{-1} \text{ cm}^{-2}$  (reference 3, p. 487), one has  $\delta_f = 2.14 \times 10^{-6} \text{ cm}$ ,  $v_0\tau = 3.82 \times 10^{-6} \text{ cm}$ , and, hence,  $A_v/A_s = 0.63$ , which, with  $A_s$  equal to 0.28 percent,<sup>4</sup> gives a total absorptivity of 0.46 percent, in moderately good agreement with experiment.<sup>4</sup>

<sup>1</sup> Momentum transfer due to phonon absorption is, of course, also limited when  $T \ll \Theta$ , since only low-momentum phonons are available. This situation, in contrast to phonon emission, is not altered by the quantum-mechanical consideration presented immediately below.

<sup>2</sup> T. Holstein, Phys. Rev. **88**, 1427 (1952), Eq. (10) with  $p=0$  (diffuse reflection of electrons at the metallic boundary). In this equation  $v_0$  is the Fermi velocity.

<sup>3</sup> R. G. Chambers, Proc. Roy. Soc. (London) **A215**, 481 (1952).

<sup>4</sup> M. A. Biondi, preceding Letter [Phys. Rev. **96**, 534 (1954)].

## Electron Groups in the Helium Negative Glow

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**D**ETAILED examination of the electron energies in the negative glow of a helium discharge at pressures of the order of 1 mm of mercury has been made with the aid of screened probes. These are similar to the type developed originally by Boyd<sup>1,2</sup> but differ in constructional details. The probes can be rotated and moved radially across the discharge.

The screened probe consists basically of a positive collecting electrode in front of which is placed a fine