The spectral response of a typical cell is shown in Fig. 1. The peak in the red is interesting in that it is a region of considerable transparency.[2] This peak has been observed on all crystals with various types of electrodes. In some crystals the peak in the red is so pronounced it masks the peak in the green. This observed peak in the red may be explained on the basis of the conduction mechanism proposed by Brosser, Kallmann, and Warminsky.[2] It appears that by proper control of impurities the spectral response can be tailor-made within limits.

In measuring the spectral response it was observed that for some crystals the short-circuit current at a given wavelength grows or decays with time depending on the wavelength of the previous illumination. Under illumination of chopped white light (up to 18 000 interruptions per second), the voltage trace as observed on an oscilloscope retained the same shape although reduced in amplitude at the higher frequencies. This reduction may have been due to a capacitance effect.

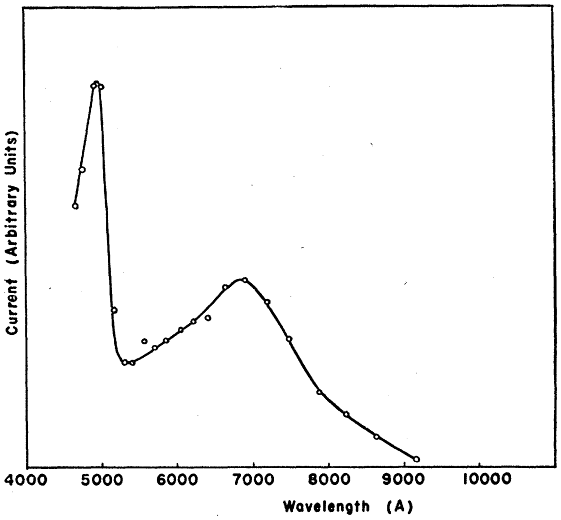

FIG. 1. Spectral photovoltaic response of CdS crystal with silver and indium electrodes.

With increasing intensity of illumination, the short-circuit current and the open-circuit voltage increased in such a manner as to give a linear increase of their product. Even up to intensities ten times that of sunlight, there appeared no indication of current or power saturation that could not be attributed to a temperature rise.

The average of all the crystals tested showed that the open-circuit voltage at room temperature dropped to half its value at approximately 150°C; and the closed-circuit current dropped to 80 percent of its room temperature value at approximately 150°C.

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[1] Czyzak, Craig, McCain, and Reynolds, J. Appl. Phys. **23**, 932 (1952).

[2] Brosser, Kallmann, and Warminsky, Z. Naturforsch. **4a**, 631 (1949).

Optical and Infrared Absorption of Copper at 4.2°K

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RECENTLY, a number of theories have been published[1–3] concerning the anomalous skin effect in metals. These theories treat the case in which the electronic mean free path is large compared to the skin depth of penetration of an electromagnetic field, and hence the absorptivity of the metal is not properly described by conventional theory.[4] Under these circumstances, the conduction electrons in the metal no longer make collisions in traversing the skin-depth region but collide only with the surface of the metal. The theories predict a different absorption of energy depending on whether the electrons are specularly or diffusely reflected from the surface of the metal. Holstein[2] has shown that in the high-frequency region (visible and infrared frequencies) if a fraction p of the electrons are specularly and $(1-p)$ are diffusely reflected from the surface, the absorptivity for normal incidence radiation is given by

$$A = A_{\text{spec}} + A_{\text{diff}} = p\frac{2\pi n e^2}{m^*\omega^2}\frac{v_0^3}{c^3} + (1-p)\frac{3}{4}\frac{v_0}{c}, \qquad (1)$$

where v_0 is the Fermi velocity and m^* and n are the effective mass and density of the electrons, respectively. Ramanathan[5] has measured the absorptivity of an electropolished copper surface at 4°K for room temperature radiation ($\lambda \sim 14\,\mu$) and finds $A=0.0062$, which is in order of magnitude agreement with the theory for $p=0$ (diffuse reflection).

In order to provide a more extensive test of the theory, an experiment was devised to measure the absorptivity as a function of the wavelength of the impinging radiation from $\lambda=0.5\,\mu$ to $\lambda=4\,\mu$. The principle of the measurements is illustrated in Fig. 1. Radiation of the desired wavelength is incident on a copper target which is mounted on a stage carrying a resistance thermometer and a heater winding. The stage is connected through a heat leak to the helium bath. The radiation reflected from the copper target is absorbed by the gold-black absorber stage,[6] which also carries a resistance thermometer and a heater winding.

With the radiation turned on, the target and absorber stages reach an equilibrium temperature somewhat in excess of the bath temperature. The changes in resistance of the thermometers imbedded in the target and the absorber stages are noted. With the radiation off, power is applied to the heater in each stage to produce the resistance change noted with the radiation on. By measuring the heater power applied to each stage, one can determine the absorptivity of the copper target.

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 ∼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 λ. The rapid rise in absorptivity at $\lambda \leq 0.55\,\mu$ is ascribed to direct interzonal transitions within the conduction band.[7] 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.[8]

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 λ 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[3] 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[9] has recently investigated the two-stage volume process in which a conduction electron absorbs a photon with 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.[9]

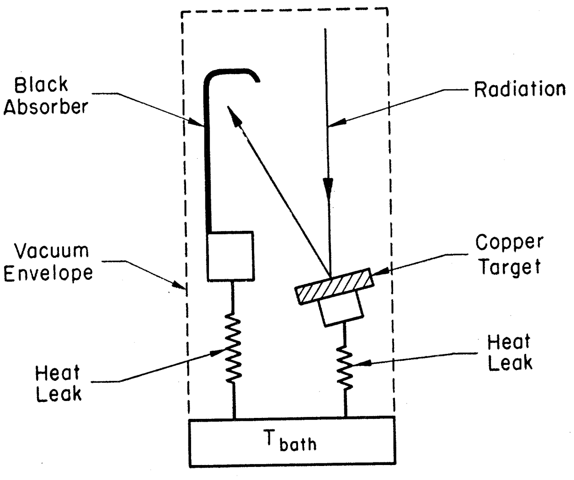

FIG. 1. Schematic diagram of the apparatus. The target and absorber stages each carry a resistance thermometer and a heater winding.

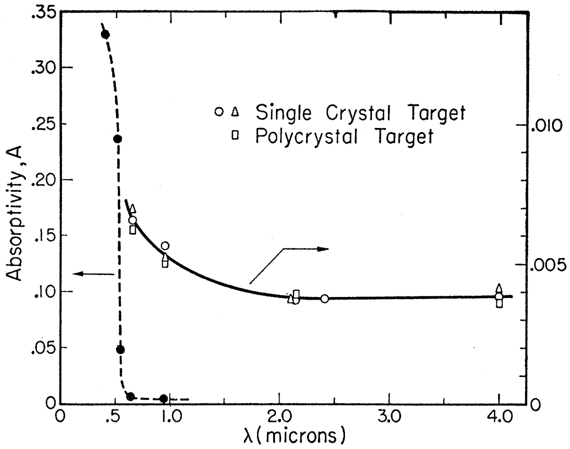

FIG. 2. Absorptivity of copper measured at 15° angle of incidence. Runs taken on the single crystal target on successive days are indicated by the symbols ○ and △. The "free' electron absorption ($\lambda > 2\mu$) is 0.0039 (corrected to normal incidence). The scale for the solid curve is at the right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

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.

The author is indebted to various members of the Low Temperature Group and the Physics Department for their considerable advice and assistance. In particular, he wishes to thank A. Wexler, who contributed greatly to the design of the experiment.

[1] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 33 (1948).

[2] T. Holstein, Phys. Rev. **88**, 1427 (1952).

[3] R. B. Dingle, Physica **19**, 311, 348 (1953).

[4] See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1936), Chap. V.

[5] K. G. Ramanathan, Proc. Phys. Soc. (London) **A65**, 532 (1952).

[6] The measured absorptivity of the gold black is $A > 0.99$.

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

[8] Hall, Bardeen, and Blatt, Phys. Rev. **95**, 559 (1954).

[9] 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