

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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(Received July 6, 1954)

**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

mesh grid to which a variable retarding potential can be applied. The fundamental advantage of a probe of this type is that it is possible to separate the positive ion component of current from the electron component directly, and thus avoid the uncertain extrapolation of the high energy part of the curve which is necessary in the analysis of the characteristic of an unscreened Langmuir probe. This particular feature of the screened probe has been used to study the "primary" electron component, which can now be measured with considerable accuracy.

By using this improved technique it has been definitely established that in the negative glow region of an abnormal glow discharge in helium there exist three distinct electron groups of differing mean energies, but each having a Maxwellian distribution: this confirms and extends earlier work by Emeléus and his group.<sup>3,4</sup> The axial variation in the concentration and temperature of the three groups taken with the probe grid facing the cathode of the discharge is reproduced in Fig. 1. It

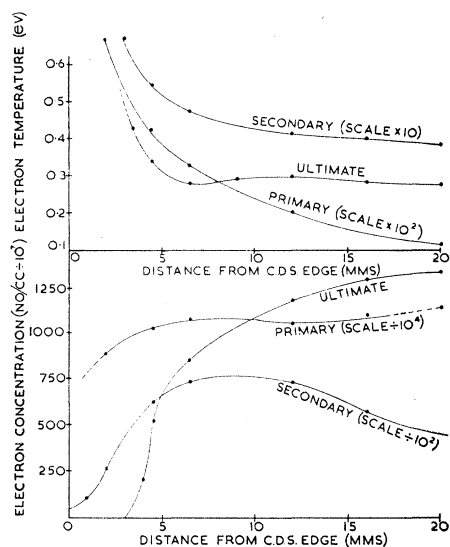


FIG. 1. Electron groups in a 600- $\mu$ A discharge in 0.58-mm helium. The probe is facing the cathode in the negative glow. (C.D.S. means cathode dark space.)

will be noted that the temperature of the primary or fastest group falls rapidly on moving into the negative glow from the cathode dark space edge while the concentration of this group varies little over the greater part of the negative glow. The directivity of the primary group is established by its failure to be detected when the probe grid is rotated so that it faces the anode: these electrons appear to have originated near the cathode, and to have been accelerated right across the cathode dark space. The "ultimate" or slowest group of electrons, which also has the highest number density, is only detectable after moving some way into the glow. When the probe grid faces the anode, however, the concentration of both this group and the inter-

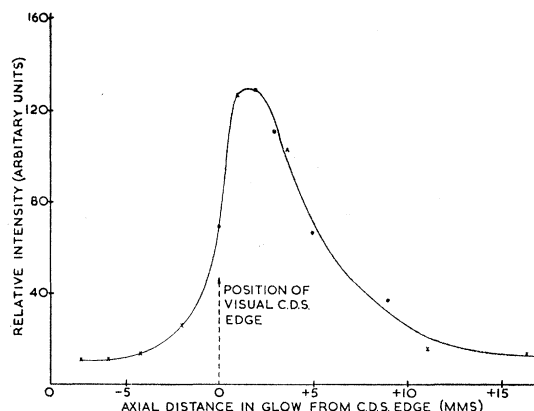


FIG. 2. Relative intensity vs axial distance in glow for the line  $\lambda=3888.6\text{\AA}$  ( $2^3S-3^3P$ ).  $\times$ — $\times$  Experimental spectroscopic points.  $\bullet$ — $\bullet$  Calculated from screened probe data and excitation probability values.

mediate or "secondary" group is considerable at the cathode dark space (C.D.S.) edge and electrons from these slow groups are detectable even a few millimeters into the dark space. Comparison of the two sets of results thus indicates the presence of a considerable drift of low-energy electrons from the region of maximum concentration, a few millimeters into the glow, towards the cathode dark space. This drift will be maintained by the electron concentration gradient in this region and by the field, for there was found to be a pronounced maximum in the space potential curve near the cathode dark space edge.

The physical interpretation of the existence of the two slow electron groups has been the subject of previous discussion. The suggestion advanced by Emeléus and Brown that their existence might be associated with the presence of a minimum in the Ramsauer electron free paths is not valid in the case of helium at this pressure, where no such minimum occurs. A more likely explanation is that the secondary group of electrons are those which have been ejected after collision between the fast primaries and gas atoms, and that they have not had time to reach thermal equilibrium with the slower "ultimate" group which are produced by the degeneration of primary and secondary groups in successive collision to very low energies, before removal by diffusion to the walls. Some support for this picture is provided by the form of the screened probe results.

Agreement has been obtained between spectrophotometric measurements of the relative intensities of the helium spectral lines and the intensities derived from the screened probe data by using Lees<sup>5</sup> figures for the excitation probabilities. Figure 2 shows a mean curve for the relative intensity of the line 3888.6 $\text{\AA}$  ( $2^3S-3^3P$ ) as a function of axial position in the negative glow. The two sets of points are seen to be in quite good agreement. No impurity or He II lines were detectable in the helium spectrum observed.

A more complete account of these experiments and results is in preparation.

<sup>1</sup> R. L. F. Boyd, Proc. Roy. Soc. (London) A201, 329 (1950).

<sup>2</sup> R. L. F. Boyd, Nature 165, 228 (1950).

<sup>3</sup> K. G. Emel us and W. L. Brown, Phil. Mag. 7, 17 (1929).

<sup>4</sup> Emel us, Brown, and Cowan, Phil. Mag. 17, 146 (1934).

<sup>5</sup> J. H. Lees, Proc. Roy. Soc. (London) A137, 173 (1932).

## Photoelectric Emission in the Extreme Ultraviolet

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(Received June 1, 1954; revised manuscript  
received August 2, 1954)

EXPERIMENTAL studies on photoelectric emission from various metals for quantum energies up to 21.2 ev show general features which led the author to the conclusion that the common "free electron"- "surface effect" picture cannot even qualitatively account for the photoelectric phenomena at higher photon energies. These features are:

1. The number of electrons emitted per incident photon (yield  $Y$ ) starts rising very steeply as soon as the quantum energy increases beyond a certain value ( $\mu$ ) which is appreciably higher than the work function ( $\phi$ ). With further increase of quantum energy,  $Y$  reaches a flat maximum followed by a slow decrease. These yields<sup>1</sup> for  $h\nu > \mu$  are, by several orders of magnitude, greater than the highest ones known from the many studies at longer wavelengths.

2. The energy distribution curves of emitted electrons practically cut off at  $E_1 = h\nu - \mu$  and not at the usually much higher maximum  $E_s = h\nu - \phi$  related to the common surface effect.<sup>2</sup>

3. There is a surprising insensitivity to some changes in the surface condition and to exposure to air.

4. Higher temperatures generally seem to reduce the number of electrons of only the lowest energies. This "true" temperature effect appears to cause only a small change in the total emission and should be clearly distinguished from larger, essentially irreversible changes of  $Y$  during the first outgassing cycle, and also from possible, closely reproducible types of an "apparent" temperature dependence which may disappear after a sufficient increase in temperature.

The following theoretical model seems to offer a reasonable interpretation of the above phenomena: For sufficiently high photon energies, most of the electron emission originates inside the metal ("volume effect") by removal of an electron from an energy level  $\mu$  (below vacuum potential). This level is supposed to represent electrons which are much more strongly bound than could be attributed to ordinary conduction

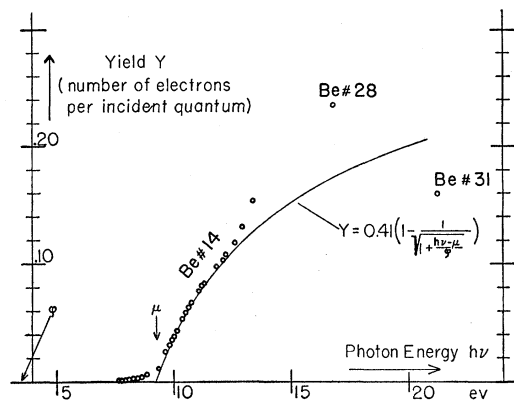


FIG. 1. Photoelectric yields of beryllium.

electrons, thus offering a high cross section for "photo-ionization." The same primary process is considered responsible for absorption of the primary radiation. Assuming, as a first approximation, that all the emitted electrons come from one definite level  $\mu$ , neglecting secondary effects of any kind, and assuming a constant coefficient  $D$  for electron transmission through the surface, one can predict the wavelength dependence of the yields. The total number of photoelectrons from level  $\mu$  should be

$$Y = 0.5D\{1 - [1 + (h\nu - \mu)/\phi]^{-1}\} \text{ per incident photon.}$$

The derivation of this equation may be briefly outlined as follows: Escape of an electron through the surface is possible only when the kinetic energy related to its component of momentum normal to the surface is equal to or greater than the work function  $\phi$ . This defines a maximum angle to the normal,  $\alpha$ , beyond which no escape can be expected, determined by the relation  $(h\nu - \mu) \cos^2 \alpha = \phi$ . The ratio of the corresponding solid angle to the total solid angle represents the probability of escape under the assumptions of ideal random distribution of the original directions inside the metal, no absorption along the way to the surface and  $D = 100$  percent. For  $h\nu - \mu \gg \phi$  and  $D = 100$  percent the maximum possible yields would be 50 percent, independent of wavelength and nature of metal. The solid curve in Fig. 1 represents the above function for  $\mu = 9.2$  ev,  $\phi = 3.7$  ev and  $D = 80$  percent and is compared with experimental data for outgassed beryllium.

The energy distribution of emitted electrons, cutting off at  $E_1 = h\nu - \mu$ , is expected to show relatively high numbers of lower energy electrons extending down to  $E = 0$  because of collisions. There is also an interesting possibility that secondary radiation of maximum quantum energy  $h\nu' = \mu - \phi$  (emitted when a vacancy in level  $\mu$  is filled by a conduction electron of maximum Fermi-energy) causes a regular photoelectric surface effect whenever  $\mu > 2\phi$ . This should contribute a subgroup with a maximum energy  $E_2 = \mu - 2\phi$ . For  $h\nu - \mu > \phi$ , the primary may cause emission of a secondary