JANUARY, 1933 REVIEWS OF MODERN PHYSICS VOLUME 5

Recent Developments in the Study of the External Photoelectric Effect

LEON B. LINFORD,* *Palmer Physical Laboratory, Princeton University*

TABLE OF CONTENTS

I. Introduction

II. General Theories of the Photoelectric Effect

III. Special Photoelectric Phenomena

I. INTRODUCTION

ANY process whereby an electron absorbs an incident quantum of radiation, thereby receiving sufficient energy to free itself from its constraints may be said to be a photoelectric effect. The electrons thus set free may move in a suitable electric circuit and produce a current which would not flow in the absence of radiation. Depending on the nature of the incident radiation and on the absorber, the processes and the resulting effects differ greatly. For convenience they may be classified as follows:

(1) The external photoelectric effect. The ejection of electrons from surfaces (mostly metallic) by visible, ultraviolet or infrared radiation.

(2) The x-ray photoelectric effect. The ejection of electrons by Roentgen rays.

(3) Photoionization. Ejection of electrons from gases or vapors.

(4) Photoconductivity. Freeing of electrons within certain insulators by light, so that they become conducting.

(5) The "Sperrschicht" photoelectric effect. The ejection of electrons from one side to the other of a rectifying boundary such as cuprous oxide formed on copper.

The external photoelectric effect was the first to be discovered and studied, and the present discussion will be limited to this field. No attempt will be made to make a complete survey of the great amount of work done on this subject, as this has been done in a complete and excellent manner by Hughes and DuBridge.[1] The preliminary draft of this paper was made before the book was published, and has since been revised so as to eliminate considerable duplication of material. It is more the purpose of this article to consider critically some of the better known effects in the light of quantum mechanical theories which were published after much of the previously mentioned book was written.

A. Historical

While experimentally investigating Maxwell's electromagnetic theory of light, Hertz[2] noticed an effect which later proved to be an external photoelectric effect. He found that when the light from the spark of his primary oscillatory circuit fell on the electrodes (particularly on the negative electrode) of the spark gap of the secondary or receiving circuit the distance which the spark would jump at the second gap was increased. He showed that the effect was due to the ultraviolet light,

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* National Research Fellow in Physics. Now in Departments of Mathematics and Physics, Utah State Agricultural College.

[1] A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, McGraw Hill, New York (1932).

[2] H. Hertz, Ann. d. Physik 31, 983 (1887).

and not to visible light or to electrical effects. Hallwachs[3] found that metals insulated from ground became negatively charged when exposed to ultraviolet light, and thus associated this effect with the emission of negative electricity. Because of his work, the external photoelectric effect is sometimes called the Hallwachs effect. Lenard[4] and J. J. Thomson[5] showed that the emitted particles were the same as the cathode rays of a Geissler tube and thus that the effect was the emission of electrons.

The first theoretical advance was made by Einstein[6] in 1905 when he postulated that light must be absorbed as well as emitted in quanta of energy $h\nu$, and thus if one quantum be absorbed by one electron the following relation must hold:

$$h\nu-\epsilon_0=\tfrac{1}{2}mv_{\max}^2=eV_{\max}. \qquad (1)$$

Here ν is the frequency of the incident light; h is Planck's constant; ϵ_0* is the minimum energy required to remove an electron from its place in the metal to field free space outside, and is called the work function of the surface; m is the mass of the electron; $v_{\max}$ is the velocity of the fastest ejected electrons; and $V_{\max}$ is the retarding potential in e.s.-units required to stop the fastest electrons. This equation was satisfactorily verified several years later by the work of Hughes,[7] Compton,[8] Richardson and Compton,[9] and Millikan.[10]

The frequency ν_0 of light which will just eject electrons, but with zero velocity is called the threshold frequency and is defined by

$$h\nu_0=\epsilon_0. \qquad (2)$$

The wave-length λ_0 corresponding to the threshold frequency is called the long wave-length limit.

B. General experimental facts

To describe completely the photoelectric properties of a surface, it is necessary to know its threshold frequency; its spectral distribution function, or the emission per unit absorbed energy as a function of the frequency of the incident light; the velocity distribution of the ejected electrons; and how these functions vary with the temperature, the applied field and, if polarized light is used, with the orientation of the electric vector of the light.

On modern theories the electrons lose most of their energy on leaving the surface of the metal, and it would be expected that the nature of the surface would greatly affect its photoelectric properties. Experiments show that the presence of foreign substances to the extent of only a small part of a monomolecular layer may change the entire photoelectric character. One of the most difficult phases of the experimental work is obtaining and maintaining surfaces free from unwanted contamination.

The spectral distribution function (one is shown in Fig. 3) as experimentally determined is zero for frequencies less than about ν_0, rises with increasing frequency, and may have one or more maxima in the spectral region which can be studied. Characteristic of all curves is that they approach zero tangentially. This necessarily makes any direct determination of the threshold frequency from experimental data uncertain. Recent theory has shown a method of plotting data so as to remove this uncertainty.

An alternate method of determining the work function of a surface is to measure the photoelectric current reaching a collector against a retarding field. Then from the observed $V_{\max}$ and Einstein's equation one calculates the work function. In this case the current approaches zero asymptotically and thus leaves uncertainties as to the value of $V_{\max}$ and therefore the work function.

The velocity distribution of the ejected electrons is difficult to measure and especially if the direction is to be taken into account. Except for thin films of metal, the energy distribution function has not been treated theoretically with much

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[3] W. Hallwachs, Ann. d. Physik **33**, 301 (1888).

[4] P. Lenard, Wien. Ber. **108**, 649 (1899); Ann. d. Physik **2**, 359 (1900).

[5] J. J. Thomson, Phil. Mag. **48**, 547 (1899).

[6] A. Einstein, Ann. d. Physik **17**, 132 (1905).

* ϵ_0 is expressed in ergs per electron. For convenience in photoelectric formulas, energies will be in ergs per electron or per quantum. To change to electron volts multiply by $(c/10^8e)pq=(6.288\pm0.006)\times10^{11}$ where pq is the factor for changing from absolute to international volts (R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929)).

[7] A. L. Hughes, Phil. Trans. Roy. Soc. **212**, 205 (1912).

[8] K. T. Compton, Phil. Mag. **23**, 579 (1912).

[9] O. W. Richardson and K. T. Compton, Phil. Mag. **24**, 575 (1912).

[10] R. A. Millikan, Phys. Rev. [2] **7**, 355 (1916).

success. Such factors as collisions of the excited electrons before leaving the metal and the effect of the finite structure of the metal surface make a theoretical treatment with present methods almost impossible.

Much interesting information about the photoelectric effect can be obtained from photoelectric surfaces consisting of films on some suitable base. In addition, many new problems arise in connection with such surfaces. The materials used for these films are usually alkali or alkaline earth metals alone or in combination with other substances, usually dielectrics. The most frequently used dielectrics are hydrogen and oxygen. The outstanding characteristics of these composite surfaces are low work function and high photoelectric efficiency, or large emission per unit absorbed energy. These characteristics are the ones desired in photoelectric cells for technical and commercial purposes.

Elster and Geitel[11] showed that alkali films produced very sensitive photoelectric surfaces. These surfaces have been studied in great detail by Elster and Geitel, Ives and coworkers, and by Suhrmann and Theissing. They found[12, 13] that with increasing thickness of film the work function changed continuously from the value for the base metal to a minimum, less than either metal alone, and finally increased to the value for the solid alkali. Brady[14] found for potassium, rubidium and caesium on silver, that the minimum work function occurred when the film was 1 to 2 atoms deep, that maximum emission occurred when films were about 5 atoms thick and that films more than 12 atoms thick had the characteristics of the solid metal. These thicknesses were determined by distilling the alkali metal onto the silver surface at a known rate.

Ives and Olpin[12] found that the minimum work function, reached by an alkali metal film as it forms on a clean surface, is equal to the resonance potential of that metal. This means that the minimum threshold frequency is equal to the frequency of the first line of the principal series of the metal in vapor form. A satisfactory explanation of this effect has not been given.

Some of the surface films and complex surfaces show a marked spectral selectivity, which means that they show a very high photoelectric efficiency in a limited spectral range. Another characteristic which may be shown by such surfaces is vectorial selectivity, or a dependence of the photoelectric efficiency on the orientation of the electric vector of polarized light with respect to the surface. The efficiency is usually greater when a component of this vector is normal to the surface than when it is in the plane of the surface.

Finally, some of these surfaces show abnormal current voltage characteristics. If the photoelectric surface or cathode is slightly negative with respect to the collector or anode, all the emitted electrons would be expected to flow across from cathode to anode. In practice with pure metal cathodes, an accelerating potential of less than 5 volts is sufficient to produce a current which remains almost constant as the voltage is increased. This is called the saturation current. The current from some of the complex surfaces increases with the applied accelerating potential until it reaches the order of 100 volts.

II. General Theories of the Photoelectric Effect

With this short sketch of some of the outstanding experimental features of the photoelectric effect, a summary of some of the more successful general theoretical treatments will be given. Most of these general theories must of necessity be based on simple models and therefore apply only to clean surfaces for emission at absolute zero. Special refinements of the general theory as applied to particular phenomena and to complex surfaces will be discussed in the third part of this paper.

A. Classical theories

Previous to the Sommerfeld electron theory of metals, one of the best pictures of the interior of a metal was that the free electrons, about 1 per atom, formed a "gas" with a Maxwell-Boltzmann distribution of velocities. This theory accounted for the high electrical and heat conductivities of the metals, but gave too high a value for the heat

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[11] J. Elster and H. Geitel, Ann. d. Physik **42**, 564 (1891).

[12] H. E. Ives and A. R. Olpin, Phys. Rev. [2] **34**, 117 (1929).

[13] R. Suhrmann and H. Theissing, Zeits. f. Physik **55**, 701 (1929).

[14] J. J. Brady, Phys. Rev. [2] **37**, 230 (1931); [2] **39**, 546 (1932); [2] **41**, 613 (1932).

capacities. Several rather unsuccessful attempts were made to overcome this difficulty. Photoelectric theories based on the old picture were able to account for the small change in threshold frequency and emission with temperature. These results follow from the fact that the change in value of the most probable electron energy, over the temperature range used in photoelectric experiments, is small compared with the work function.

Theoretical spectral distribution functions have been calculated by Richardson,[15] J. J. Thomson[16] and Uspensky.[17] Richardson's curve meets the axis with finite slope at the threshold frequency. The other two are tangent at $\nu=\nu_0$, but all three rise more rapidly with the frequency near the threshold than the experimental curves. Richardson's equation has a maximum at $\nu=(3/2)\nu_0$ and Thomson's at $\nu=2\nu_0$. Selective maxima have been found quite generally in this region. The maximum of Uspensky's curve is at $\nu=9\nu_0$. Hughes and DuBridge[17a] point out that by varying Thomson's assumption as to the way in which the absorption coefficient for light varies with the frequency, spectral distribution functions can be obtained which fit the data well for frequencies near the threshold. These equations however have no maximum. Thus no single theory follows the experimental data over a wide frequency range.

Without any special assumptions as to the theory of metals, or the actual process of photoelectric emission Richardson[18] has given an equation for the photoelectric emission from a surface exposed to radiation from a black body, this has been called the complete emission. Richardson's equation for thermionic emission is

$$I=AT^re^{-\epsilon_0/kT}, \tag{3}$$

where I is the current density from the surface, A is a constant, T is the absolute temperature, k is Boltzmann's constant, and r is a constant and, depending on assumptions made in derivations, either $\frac{1}{2}$ or 2. The value 2 is the one obtained on the newer theory of metals, and is now accepted as correct.

Eq. (3) can be derived by determining the rate at which electrons leave a surface enclosed in a black body cavity without any assumptions as to the mechanism of the emission.[19] When the electron emitter is within the cavity the electrons may be ejected either by thermionic emission or by photoelectric emission due to the black body radiation. This is an equilibrium process and if equilibrium conditions could be maintained it would be expected that the same equation would hold if the electron emitter were elsewhere and exposed to the radiation from a black body. Deviations from this equation should be then a measure of the deviations from equilibrium conditions. Evidently the constant A would be much smaller and T would represent the temperature of the black body.

This equation has been verified experimentally by Roy[20] using black body radiation and by Suhrmann[21] who calculated the complete emission from experimentally determined spectral distribution functions. If $F(\nu)$ represents the spectral distribution function and $E\ (\nu,\ T)$ the energy distribution function of black body radiation, Planck's law, then the complete emission I_c is given by

$$I_c=\int_{\nu_0}^{\infty}F(\nu)E(\nu,\ T)d\nu. \tag{4}$$

By means of graphical integration the complete emission can be determined for various temperatures.

When I_c/T^2 was plotted against $1/T$, both Roy and Suhrmann found the lines were straight and that the slope gave a good value for the work function. Later Suhrmann[22] reported that he obtained better straight lines if r in Eq. (3) was taken as about 4 rather than 2. There seems to be no theoretical justification for this higher value.

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[15] O. W. Richardson, Phil. Mag. **24**, 570 (1912).

[16] J. J. Thomson, Phil. Mag. **2**, 674 (1926).

[17] A. W. Uspensky, Zeits. f. Physik **40**, 456 (1926).

[17a] See page 200 of reference 1.

[18] O. W. Richardson, Phil. Mag. **23**, 594 (1912).

[19] For a good derivation of Richardson's equation on these assumptions, see S. Dushman, Phys. Rev. [2] **21**, 623 (1923). Richardson's equation in this form is not rigorously true if ϵ_0 is a function of temperature. For clean metals the deviations are small. This form of the equation is exact enough for the present discussion.

[20] S. C. Roy, Proc. Roy. Soc. **A112**, 599 (1926).

[21] R. Suhrmann, Zeits. f. Physik **33**, 63 (1925).

[22] R. Suhrmann, Zeits. f. Physik **54**, 99 (1928).

B. Quantum mechanical theories

(1) *The new electron theory of metals.* With the application of the Pauli exclusion principle and the resulting Fermi statistics to the free electrons in metals, Sommerfeld and others were able to formulate a new theory which would account for the electrical and heat conductivities of metals, as well as other principal characteristics, without giving too high a heat capacity. This with quantum mechanical methods gave a new and powerful method of treating the problems of emission of electrons from metals.[23]

A brief summary of some of the results of the new theory of metals will be helpful in understanding the photoelectric theories.

Consider the surface of the metal which is emitting electrons to be in the xy-plane and the outward normal the positive z-direction. Let ξ, η, ζ be the x, y, z-components of velocity of any electron. To calculate the emission from unit area of the surface it is necessary to find the number of electrons $N(W)dW$ whose normal component of energy $W=\frac{1}{2}m\zeta^2$* is between W and $W+dW$, which strike unit area of the surface in unit time; multiply this by the probability $D(W)$ that an electron with normal component of energy W will be transmitted through the surface and escape, and integrate over all values of W. Thus the current density is

$$I=\int_0^\infty N(W)D(W)dW. \tag{5}$$

On the basis of Fermi statistics the velocity distribution function of electrons in a metal is

$$f(\xi,\eta,\zeta)d\xi d\eta d\zeta$$
$$=\frac{2m^3}{h^3}\frac{d\xi d\eta d\zeta}{\exp\left(\{\frac{1}{2}m(\xi^2+\eta^2+\zeta^2)-\bar{\epsilon}\}/kT\right)+1}, \tag{6}$$

where $f(\xi,\eta,\zeta)d\xi d\eta d\zeta$ is the number of electrons per unit volume with x, y, z-components of velocity between ξ, η, ζ and $\xi+d\xi, \eta+d\eta, \zeta+d\zeta$, $\bar{\epsilon}$ is the energy of the fastest electrons of the Fermi distribution at 0°K and is given by

$$\bar{\epsilon}=h\bar{\nu}=(h^2/8m)(3n/\pi)^{\frac{2}{3}}, \tag{7}$$

where m is the mass of the electron and n the number of free electrons per unit volume of the metal. The value of $\bar{\epsilon}$ ranges from the equivalent of about 2 electron volts for the alkalies to more than 10 volts for some of the heavy metals.

The value of $f(\xi,\eta,\zeta)$ at 0°K as given by Eq. (6) is constant and equal to $2m^3/h^3$ for energies of the electron $\epsilon=\frac{1}{2}m(\xi^2+\eta^2+\zeta^2)<\bar{\epsilon}$ and for energies greater than this critical value the function is zero. For higher temperatures, $f(\xi,\eta,\zeta)$ drops from the value $2m^3/h^3$ to zero exponentially in the region $\epsilon\cong\bar{\epsilon}$ having half value at $\epsilon=\bar{\epsilon}$.

Expressed in terms of the energies of the electrons the distribution function is

$$F(\epsilon)d\epsilon=\frac{8\pi m}{h^3}\frac{(2m\epsilon)^{\frac{1}{2}}d\epsilon}{e^{(\epsilon-\bar{\epsilon})/kT}+1}. \tag{8}$$

The striking difference between the two theories is that on the classical theory the electrons are at rest at absolute zero whereas on the new theory they have energies up to the relatively large value $\bar{\epsilon}$. With increasing temperature, on the old theory all electrons take on increasing energies, whereas on the new theory only a few of the fastest increase their energy above $\bar{\epsilon}$.

Fowler[23a] used the distribution given by Eq. (8) for a preliminary theory of the photoelectric effect. It was soon pointed out that only the normal component of energy is effective in escape and Nordheim[23] calculated the required function $N(W)dW$, which is

$$N(W)dW$$
$$=(4\pi m/h^3)kT\cdot ln(1+e^{-(W-\bar{\epsilon})/kT})dW. \tag{9}$$

This can be reduced to the three approximate forms for different values of $(W-\bar{\epsilon})/kT$:

$$N(W)dW=(4\pi m/h^3)(\bar{\epsilon}-W)dW \quad \text{for} \quad (W-\bar{\epsilon})/kT\ll 0, \tag{10a}$$
$$=(4\pi m/h^3)kTdW \quad \text{for} \quad (W-\bar{\epsilon})/kT\cong 0, \tag{10b}$$
$$=(4\pi m/h^3)kTe^{-(W-\bar{\epsilon})/kT}dW \quad \text{for} \quad (W-\bar{\epsilon})/kT\gg 0. \tag{10c}$$

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[23] L. Nordheim, Phys. Zeits. **30**, 177 (1929) gives an excellent discussion of the theory of metals, thermionic and autoelectronic emissions, and a review of the early theories of the photoelectric effect.

* Although energy cannot have a component in the strict sense of the word, the value of W as defined and not the total kinetic energy $\epsilon=\frac{1}{2}m(\xi^2+\eta^2+\zeta^2)$ determines whether or not the electron can leave the surface. For convenience in writing, the above terminology will be used, as is usual in treating this subject.

[23a] R. H. Fowler, Proc. Roy. Soc. **A118**, 229 (1928).

At absolute zero these reduce to

$$N(W)dW = (4\pi m/h^3)(\bar{\epsilon} - W)dW \quad \text{for} \quad W < \bar{\epsilon}, \tag{11a}$$

$$= 0 \qquad\qquad \text{for} \quad W > \bar{\epsilon}. \tag{11b}$$

The difference in form of the two functions is shown in Fig. 1 where they are sketched for both absolute zero (solid line) and for a temperature about 1000°K (broken line). W and ϵ are plotted on the same scale, but the ordinates $F(\epsilon)$ and $N(W)$ are on entirely different scales.

In order to determine the transmission coefficient[24] $D(W)$ for a surface, a particular form of potential barrier retaining the electrons in the metal must be chosen, and then the wave function set up for the electrons both inside and out of the metal. A common method is to write the wave function normalized for unit current density moving normally toward the surface from within the metal; then set up functions with undetermined coefficients to represent the transmitted beam leaving the metal, and the reflected beam returning to the interior. The coefficients must be so adjusted that the total wave function and its first derivative be continuous everywhere. These conditions are sufficient to determine the coefficients of the terms representing the transmitted and reflected beams. The transmission coefficient is the square of the absolute magnitude of the coefficient of the term representing the transmitted beam, since the corresponding magnitude for the incident beam has been normalized to unity. The resulting transmission coefficient as a function of the normal energy W of the electron is dependent on the form of the potential barrier chosen.

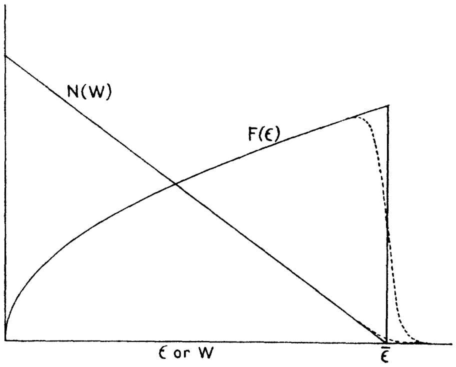

Fig. 1. Fermi distribution functions for electrons at absolute zero (solid lines) and 1000°K (broken lines). $F(\epsilon)d\epsilon$ is the number of electrons with energy between ϵ and $\epsilon+d\epsilon$. $N(W)dW$ is the number of electrons with normal component of energy between W and $W+dW$ which strike unit area of the surface in unit time.[*]

The simplest form of potential barrier at a metallic surface is an abrupt rise of potential to its value at infinity, OAB (Fig. 2). A potential which more nearly corresponds to the actual case is

$$V = h\nu_a - e/4z \quad \text{for} \quad z > z', \tag{12}$$

which is obtained if it be assumed that for distances greater than z' (of the order of atomic dimensions) the emerging electron is subject to the force due to its own image in the metal. This potential curve is shown by ODB (Fig. 2). In both cases the difference in potential between the

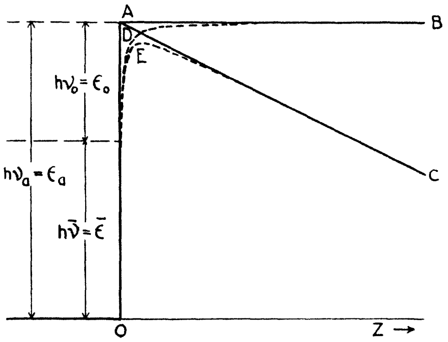

Fig. 2. Two types of surface potential barrier, showing the effects of an accelerating field. OAB is a step-like barrier in zero field and OAC in accelerating field. ODB and OEC are the corresponding barriers for an image field.

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[24] Besides the review of the early work on this subject in reference 23, a more recent and detailed discussion is given by E. U. Condon, Rev. Mod. Phys. **3**, 43 (1931). Among the more recent articles may be mentioned N. H. Frank and L. A. Young, Phys. Rev. [2] **38**, 80 (1931); W. Wetzel, Phys. Rev. [2] **38**, 1205 (1931); and V. Rojansky and W. Wetzel, Phys. Rev. [2] **38**, 1979 (1931).

[*] It is impossible for $N(W)$, see Eq. (9), at $T > 0$°K to be less than it is at $T = 0$ for any particular value of the normal component of energy W. The area under this curve is the number of electrons striking the surface per second and this must increase with the temperature. Nordheim[23] sketched the curve for $T > 0$ so that it dropped below the curve for $T = 0$ at a value of W somewhat less than $\bar{\epsilon}$, and then approached the $T = 0$ curve from below, as W decreases. A similar error has been made by other writers.[1, 47]

interior of the metal and field free space outside is $h\nu_a = \epsilon_a$. From previous discussion it is evident that ϵ_a is the sum of $\bar{\epsilon}$, the energy of the fastest electrons of the Fermi distribution, and ϵ_0 the work function which is the energy needed to take an electron with energy $\bar{\epsilon}$ to field free space outside the metal. Or

$$\epsilon_a = \bar{\epsilon} + \epsilon_0; \qquad h\nu_a = h\bar{\nu} + h\nu_0. \tag{13}$$

Calculations by Nordheim and others show that for both barriers $D(W) = 0$ for $W < h\nu_a$ and $D(W)$ rapidly approaches unity for $W > h\nu_a$. For $W - h\nu_a$ corresponding to 0.1 electron volt $D(W) > 0.99$.

If an accelerating field is applied to the surface, the potential barrier OAB becomes OAC, and ODB becomes OEC. In the former case the applied field does not affect the maximum height of the barrier whereas in the second case the height of the barrier and thus the effective work function is decreased. As in the case of no external field $D(W) \to 1$ for W greater than the maximum height of the barrier, but in this case for W less than the maximum height of the barrier, $D(W)$ remains finite though small. This probability that an electron will be transmitted through a region where its classical energy would be negative, from one classically allowed region to another, accounts for the emission of electrons from cold metals under intense fields, as well as some other phenomena which could not be accounted for on classical theory.

By substituting the values of $N(W)dW$ and of $D(W)$ into Eq. (5) and integrating over proper limits, both Richardson's thermionic equation and the experimentally determined equation for the autoelectronic effect can be derived.

The problem of photoelectric emission is more complicated, as one must calculate the effect of the incident light on the velocity distribution of the electrons, and use this new function to determine the emission. The following are the essential steps: (1) Set up the equation for the light in the metal. (2) Determine the probability that an electron with velocity components ξ, η, ζ will absorb a quantum of light of frequency ν so that the electron will have a final component of energy, normal to the surface, W'. (This will involve among other factors ξ, η, ζ, ν, the intensity and polarization of the light, and the nature of the electrostatic field in the neighborhood of the electron.) (3) Calculate $N'(W')dW'$, which is the number of excited electrons with energies normal to the surface between W' and $W' + dW'$ which strike unit area of the surface in unit time. The emitted current density will be

$$I = \int_0^\infty N'(W')D(W')dW'. \tag{14}$$

So far it has been impossible to obtain an exact solution on this scheme, so the present theories are the results of various methods of approximation. Some of the better ones will be outlined briefly.

(2) *Wentzel's formulation.* Wentzel[25] made the first solution in which the interaction of the radiation and electrons was treated quantum mechanically. He assumed the free electrons in a rectangular block of metal with sides $l_1\ l_2\ l_3$ and set up the wave equation in the box as

$$\psi_0 = u_0 e^{(2\pi i/h)(mc^2+\epsilon)t} \tag{15a}$$

where

$$u_0 = (8/l_1 l_2 l_3)^{\frac{1}{2}} \sin k_1 x \sin k_2 y \sin k_3 z \tag{15b}$$

$$k_j = \pi n_j / l_j; \quad j = 1, 2, 3; \quad n_j = 1, 2, \cdots \tag{15c}$$

$$\epsilon = h^2 k^2 / 8\pi^2 m; \quad k^2 = k_1^2 + k_2^2 + k_3^2. \tag{15d}$$

ϵ is here the kinetic energy of the electron before excitation by the light. He then assumed that the light is classically damped inside the metal with the extinction coefficient α and thus the electric vector of the light wave in the metal where the coordinate z is negative, is given by the formula

$$E = E_0 e^{\alpha z}[\cos 2\pi i\nu t - (\mathbf{Kr})]. \tag{16}$$

By this assumption he tried to overcome the difficulty arising from conservation of momentum considerations. The point will be discussed in greater detail in connection with Tamm and Shubin's theory.

Wentzel applied the electric vector as a perturbation on the wave equation of the electrons, Eq. (15a), and obtained the new wave function

$$\psi = \psi_0 + \psi_1. \tag{17}$$

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[25] G. Wentzel, in Sommerfeld's 60. Geburtstag Festschrift, Probleme der Modernen Physik, edited by P. Debye, p. 79, Leipzig (1928).

The first order perturbation term ψ_1 is given by the equation

$$\frac{h^2}{8\pi^2 m}\Delta\psi_1+\frac{h}{2\pi i}\frac{\partial\psi_1}{\partial t}-mc^2\psi_1 =\frac{eh}{8\pi m\nu}e^{\alpha z-i(\mathbf{Kr})-2\pi i\nu t}\cdot(E_0\,\mathrm{grad}\,\psi_0). \quad (18)$$

From the theory $|\psi_1|^2$ gives the probability that an electron with initial energy ϵ will absorb a quantum of energy $h\nu$. This must be integrated over the volume and summed for all initial energies ϵ.

He then assumed that all electrons with energy sufficient to escape would do so regardless of their direction of motion, thus that the transmission coefficient D is unity for $\epsilon+h\nu>h\nu_a$ and arrived at the result

$$I\sim[\bar{\nu}^{5/2}-(\nu_a-\nu)^{5/2}]\nu^{-7/2}E_z^2+(1/14)[\bar{\nu}^{7/2}-(\nu_a-\nu)^{7/2}]\nu^{-9/2}[3E_z^2+2E_x^2+2E_y^2]+\cdots. \quad (19)$$

E_x, E_y, E_z are the components of the electric vector, E_z being the component normal to the surface.

Houston[26] correctly pointed out that only those electrons which, after the last collision in the metal, have an energy component normal to the surface greater than ϵ_a can escape. He arrived at the formula

$$I\sim\left(\frac{\bar{\nu}}{\nu}\right)^{\frac{1}{2}}\left\{\frac{E_z^2}{\nu}\left[1+\frac{\bar{\nu}}{2\nu}\right] +\frac{E_x^2+E_y^2}{3\nu}\left[\frac{\nu-\nu_0}{\nu}\right]\right\}\left(\frac{\nu-\nu_0}{\nu}\right)^2. \quad (20)$$

Wentzel[27] recalculated his formula on the basis of Houston's correction and obtained

$$I\sim\nu^{-7/2}\{(1/3)\bar{\nu}[\bar{\nu}^{3/2}-(\nu_a-\nu)^{3/2}] -(1/5)[\bar{\nu}^{5/2}-(\nu_a-\nu)^{5/2}]\}E_z^2+\cdots. \quad (21)$$

Although Eqs. (21) and (22) are quite different in form, the distribution curves they represent are similar.

The essential characteristics of the spectral sensitivity curves as given by Eqs. (20) and (21) are: (1) The curves leave the axis at $\nu=\nu_0$ at a finite angle; (2) rise to a maximum for the frequency $\nu_{\max}$ in the range $\nu_a>\nu_{\max}>\nu_0$; (3) the equations show that E_z is more effective in ejecting electrons than E_x or E_y. Although these sensitivity curves meet the axis at a finite angle at $\nu=\nu_0$, their shape for greater frequencies is very near that of the experimental curves.

(3) *Fröhlich's theory for thin films.* Fröhlich[28] pointed out that our knowledge of the behavior of light within a metal is limited. He chose to work with a film, thin enough that the absorption of light in the metal could be neglected, and thus eliminated the term involving the absorption coefficient α from the equation for the electric vector of the light in the metal (see Eq. (16)).

He divides the space in three regions, (1) in the film, (2) outside the film, on the side of the incident light (positive z-direction), and (3) the region back of the film (negative z-direction); and derives the following wave equations for the three regions, where the film is a rectangle of sides l_1, l_2, and thickness $2l_3$:

$$(1)\quad \psi=2a\cos k_3z\sin k_1x\sin k_2y, \quad (22a)$$

$$(2)\quad \psi=be^{ipz}\sin k_1x\sin k_2y, \quad (22b)$$

$$(3)\quad \psi=be^{-ipz}\sin k_1x\sin k_2y, \quad (22c)$$

where $hk_j/2\pi m$ is the classical velocity in the x, y, or z-direction as j takes the value 1, 2 or 3, and

$$p^2=k_3^2-8\pi^2m\nu_a/h \quad (23a)$$

$$b=2a\cos k_3l_3e^{-ipl_3} \quad (23b)$$

$$a=(2l_1l_2l_3)^{-\frac{1}{2}}. \quad (23c)$$

He then allowed the light to act as a perturbation, as did Wentzel, and calculated the number of electrons which are excited to energies and directions such that they can escape from the surface and obtained the following equations.

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[26] W. V. Houston. As quoted on page 495 by E. O. Lawrence and L. B. Linford, Phys. Rev. [2] 36, 482 (1930).

[27] See page 496 of reference 26.

[28] H. Fröhlich, Ann. d. Physik 7, 103 (1930).

For $\nu_0<\nu<\nu_a$

$$I=(e^2\nu_a{}^2\bar{\nu}E_z{}^2/16\pi h^2)\nu^{-4}\{A_1((\nu-\nu_0)/\nu_a)+A_2((\nu-\nu_0)/\nu_a)^2+\cdots\}$$

where

$$\left.\begin{aligned}A_1&=-\frac{7\nu_0}{\nu_a}+\left(\frac{21}{2}-\frac{7}{2}\frac{\bar{\nu}}{\nu_a}\right)\frac{\nu}{\nu_a}-\left(\frac{21}{8}+\frac{5}{4}\frac{\bar{\nu}}{\nu_a}\right)\left(\frac{\nu}{\nu_a}\right)^2+\cdots\\ A_2&=\left(-\frac{11}{2}+\frac{2\bar{\nu}}{\nu_a}\right)+\left(3+\frac{3}{4}\frac{\bar{\nu}}{\nu_a}\right)\frac{\nu}{\nu_a}+\left(\frac{9}{16}+\frac{11}{8}\frac{\bar{\nu}}{\nu_a}\right)\left(\frac{\nu}{\nu_a}\right)^2+\cdots.\end{aligned}\right\}\tag{24a}$$

For $\nu>\nu_a$

$$I=(e^3\nu_a{}^2\bar{\nu}E_z{}^2/16\pi h^2)\nu^{-4}\{B_1+B_2+\cdots\},$$

where

$$\left.\begin{aligned}B_1&=\left(\frac{1}{2}\frac{\nu_a}{\bar{\nu}}-1\right)\frac{\nu}{\nu_a}+\left(\frac{5}{2}+\frac{1}{8}\frac{\nu_a}{\bar{\nu}}\right)+\left(\frac{7}{4}-\frac{3}{8}\frac{\nu_a}{\bar{\nu}}\right)\frac{\nu_a}{\nu}-\frac{3}{2}\left(\frac{\nu_a}{\nu}\right)^2+\cdots\\ B_2&=\left(-2+\frac{\bar{\nu}}{\nu}\right)+\left(\frac{15}{4}\frac{\bar{\nu}}{\nu_a}-\frac{9}{16}\right)\frac{\nu_a}{\nu}+\left(\frac{21}{16}-\frac{5}{8}\frac{\bar{\nu}}{\nu_a}\right)\left(\frac{\nu_a}{\nu}\right)^2+\cdots.\end{aligned}\right\}\tag{24b}$$

The general features of the spectral sensitivity curves are the same as those of Wentzel and Houston. The distribution of velocities is different. This theory predicts that the most probable energy of ejection is close to the maximum energy, with relatively few of the slow electrons. This effect was noted by Lukirsky and Prilezaev,[29] who found that the thinner the film, the more nearly did the observed energy distribution approach the form predicted by this theory.

The positions of the spectral maxima for some of the alkali metals as calculated by Fröhlich from his theory are in good agreement with the experimental values. The values of $\bar{\nu}$ were calculated on the assumption of 1 free electron per atom using Eq. (7). The values for the thresholds were not the best now available, but were of proper order of magnitude. The frequency for maximum emission $\nu_{\max}$ as calculated was within 10 percent of the observed values. The most convincing agreement was for potassium where the data for the threshold and spectral maximum were taken from one spectral distribution curve for a distilled film of potassium on platinum reported by Suhrmann and Theissing.[13] The calculated $\nu_{\max}$ was about 5 percent lower than the experimental value.

(4) *Theory of Tamm and Schubin.* Tamm and Schubin[30] independently made essentially the same calculations as did Fröhlich and carried them further. In addition their interpretation of many of the results is better. They point out that an electron in field free space cannot absorb all the energy of a light quantum and at the same time conserve both energy and momentum. If the electron is in an electric field, momentum can be transferred by means of the field to its source, or in this case to the metal lattice. Because of the mass of the metal ions, the excess momentum can be transferred with little loss of energy to the ions.

There are two types of fields in which conduction electrons may be found. One is the field of the potential barrier at the surface of the metal and the other is the field of the crystal lattice. Since the latter fields are small compared with the former, the lattice or volume effect can be neglected in calculating the effect due to the surface potential barrier or the surface effect.

The method Wentzel used to satisfy momentum conditions is not free from criticism. It is true that a uniformly damped wave can be expanded in a Fourier series such that formally the conservation of energy and momentum in a photoelectric process can be satisfied. Tamm and Schubin[30] and later Bloch [31] call attention to the fact that the absorption of light in a metal is principally photoelectric, and therefore essentially a discontinuous process. The effect of the discontinuity in the absorption of light on the results of the theory is difficult to determine, so it is preferable to have a theory free from this defect.

Since Fröhlich assumed no damping of the electric vector of the light and that the electrons

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[29] P. Lukirsky and S. Prilezaev, Zeits. f. Physik **49**, 236 (1928).

[30] I. Tamm and S. Schubin, Zeits. f. Physik **68**, 97 (1931).

[31] F. Bloch, Phys. Zeits. **32**, 881 (1931).

were free in the metal, his result gives the emission due to the surface effect. Tamm and Schubin call attention to the error in Fröhlich's proposed extension for solid metals by summing up the effect for each layer with an absorption coefficient for both the light and electrons. Such a process would assume surface type excitation in the interior of the metal. They recalculate the surface emission for a thick block of metal and obtain

$$I=(e^2\nu_a|E_z|^2/2ch^2\nu^4\cos\theta)\{(\nu\Delta)^{\frac{1}{2}}(3\Delta-\bar{\nu})$$
$$-(\Delta-\bar{\nu})(3\Delta+\bar{\nu})\ln[(\nu^{\frac{1}{2}}+\Delta^{\frac{1}{2}})/(|\Delta-\bar{\nu}|^{\frac{1}{2}})]\} \quad (25)$$

where $\Delta=\nu-\nu_0$ and θ is the angle of incidence of the light. The shape of this spectral distribution function, Eq. (25), is similar to that experimentally determined by Suhrmann and Theissing[32] for thick layers of potassium.

The above correlation indicates that while only a very small part of the light is absorbed at the surface of a metal, it contributes most of the photoelectrons for frequencies near the threshold. Whereas most of the light is absorbed in the interior of the metal from which place few electrons escape. This may be due either to inelastic collisions of electrons in the metal before escaping, or to the excitation of lower energy electrons in the interior than on the surface. The latter effect would lead to a large number of electrons excited, but to an energy less than that required to escape.

To determine the conditions for absorption of light within a metal, Tamm and Schubin used the Bloch eigenfunction for electrons in the periodic field of a metal lattice.

$$\psi_{K_1,K_2,K_3}=\exp[i(2\pi\nu_{K_1,K_2,K_3}t-K_1x$$
$$-K_2y-K_3z)]\cdot u_{K_1,K_2,K_3}(x,y,z), \quad (26)$$

where $K^2=K_1^2+K_2^2+K_3^2=\gamma\nu$; $\gamma=8\pi^2m/h$ and u is a periodic function of the coordinates, with a period equal to the lattice constant. K^2 is an inverse length and proportional to the energy of the state in question.

If a quantum of energy $h\nu$ is absorbed by an electron in the state K and raised to the state k the energy equation

$$\nu_{k_1,k_2,k_3}=\nu_{K_1,K_2,K_3}+\nu \quad (27)$$

must be fulfilled. Besides this the following diffraction condition is imposed as a result of the discrete energy levels in the metal

$$k_j=K_j\pm 2\pi n_j/a \quad \begin{matrix} n=1,2,\cdots, \\ j=1,2,3, \end{matrix} \quad (28)$$

where a is the lattice constant of the metal.

The smallest frequency which can be absorbed will be given by Eq. (28) when one $n_j=1$ and the other two are zero. The lowest frequency ν_0' which can give electrons of energy $h\nu_a$ consistent with the above conditions is

$$\nu_0'=2(\nu_1\nu_a)^{\frac{1}{2}}-\nu_1, \quad (29)$$

where

$$\nu_1=4(\pi/3)^{2/3}\bar{\nu}. \quad (30)$$

This gives a second threshold frequency ν_0' which can be called the threshold for the volume effect. It happens that with many metals it is a little less than twice the threshold for the surface effect and for the alkalis at a frequency higher than the first maximum of the spectral distribution curve. The volume threshold is not sharp nor can its position be predicted accurately, there being a small volume effect for frequencies between the surface and volume thresholds. At frequencies greater than the volume threshold, the emission from the interior of the metal, if large enough, will cause a secondary rise in the spectral distribution function. This effect has been found on alkali metal surfaces. Fig. 3 from

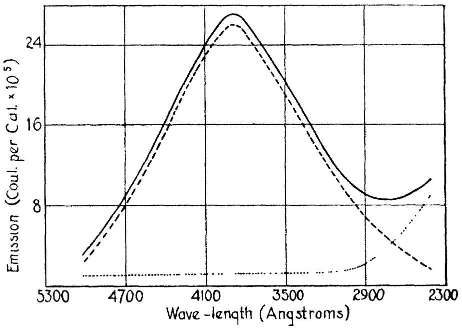

FIG. 3. How the observed spectral distribution function might be built up by the surface effect (broken line) and the volume effect (dotted line). The solid line shows the emission observed by Suhrmann and Theissing from a thick potassium film. (Tamm and Schubin.)

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[32] R. Suhrmann and H. Theissing, Zeits. f. Physik 52, 453 (1928).

Tamm and Schubin shows how the observed spectral distribution functions would be built up on their theory from a surface effect (broken line) and a volume effect (dotted line). The solid line is from the data of Suhrmann and Theissing[13] for a thick potassium film.

(5) *Penney's theory.* Penney[33] attempted a more exact formulation for the emission from a thin film by using a model with lattice structure and introducing an absorption coefficient for the light in the film. The most striking result was the prediction of sets of discrete energy levels and bands of allowed electron energies separated by energy values not allowed. These energy bands which cannot be occupied ranged from $\bar{\epsilon}$ to above ϵ_a. The existence of such bands cannot be verified by present experimental methods. Other results are similar to those of the previous theories.

(6) *General remarks.* It appears that the work of Tamm and Schubin gives the best general theory of the photoelectric effect. While admittedly incomplete, it offers an explanation for many observed phenomena. It will be used for comparison and discussion of particular phenomena in the next section.

As a general summary of the quantum mechanical theories, the following features are evident. All theories predict a spectral distribution function which leaves the axis at $\nu=\nu_0$ with finite slope. All are based on the Fermi distribution at 0°K. They predict a maximum at a frequency such that $\bar{\nu}>\nu_{\max}>\nu_0$. Tamm and Schubin's complete theory predicts a maximum, a minimum and then a second increase. For the heavy metals this second threshold is farther in the ultraviolet than investigations have been carried. All of the theories predict that the component of the electric vector normal to the surface E_z is much more effective in ejecting electrons than are the components in the plane of the surface. To the approximation given, the formulas of Fröhlich and of Tamm and Schubin depend on E_z only.

Finally, it might be mentioned that the criticism of the theory of Tamm and Schubin raised by Frenkel,[34] and his alternate explanation for the position of the spectral selective maximum presented in the same paper have been withdrawn.[35]

III. Special Photoelectric Phenomena

Although able to account for the general features of the photoelectric effect, there are many special phenomena, especially those associted with coated surfaces, which are not explained by the general theories. Frequently some application of a quantum mechanical theory or some classical consideration is helpful in understanding specific characteristics of emission. Some of these considerations should later be incorporated in a better general theory.

A. The effect of temperature on photoelectric emission

In the quantum mechanical theories considered, the electrons were assumed to have the velocity distribution characteristic of 0°K, and the work function $\epsilon_0=h\nu_0$ was defined as $\epsilon_0=\epsilon_a-\bar{\epsilon}$. For temperatures above absolute zero there are electrons with energy greater than $\bar{\epsilon}$. Since there is no sharp upper limit to these energies to use as a characteristic energy, the definition of the work function as given above will be retained for all temperatures. As a result, electrons can be emitted by light of frequency less than the threshold frequency if the metal is above absolute zero. The work function will be said to depend on temperature only if the energy, required to release an electron whose normal component of energy is $\bar{\epsilon}$, changes with the temperature; or in other words, if ϵ_a depends on T.

While working on potassium films Lawrence and Linford[36] noted the difference between the theoretical curves of Wentzel and Houston, Eqs. (19) and (20) and the observed tangential approach to zero of the spectral distribution function. They reported that the magnitude of the difference could be explained by the temperature effect.

Recently, Fowler[37] has derived a theory which gives a different method of plotting experimental data from which the threshold for 0°K can be determined. He worked through the theory with three initial assumptions, and among other things calculated I_n the emission produced by light of the threshold frequency as a function of temperature. The assumptions were:

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[33] W. G. Penney, Proc. Roy. Soc. **A133**, 407 (1931).

[34] J. Frenkel, Phys. Rev. [2] **38**, 309 (1931).

[35] I. Tamm, Phys. Rev. [2] **39**, 170 (1932).

[36] E. O. Lawrence and L. B. Linford, Phys. Rev. [2] **36**, 482 (1930).

[37] R. H. Fowler, Phys. Rev. [2] **38**, 45 (1931).

(1) That all electrons with energy greater than ϵ_a would escape. The result for $T=0$ is similar to the first term of Wentzel's first equation, Eq. (19). He found that $I_{\nu_0}\sim T$ and that for $T>0$ the curve approached zero with finite slope. The displacement was smaller than that observed, so the result was discarded.

(2) That all electrons with normal component of energy greater than ϵ_a would escape. For $T=0$ the result was similar to the first term of Houston's equation and Wentzel's corrected formula, Eqs. (20) and (21). In this case $I_{\nu_0}\sim T^2$.

(3) Fowler then introduced a term to account for the probability of excitation, and obtained a result for $T=0$ similar to the first term of Fröhlich's formula, Eq. (24a). On this assumption $I_{\nu_0}\sim T^{3/2}$.

In the last two cases the approach of the spectral distribution curve to zero is tangential. The temperature corrections are so nearly correct that present experimental data are not sufficiently accurate to indicate either one as superior.

Young and Frank[38] suggested a different probability of escape from the surface than Fowler's third assumption, which formulation leads to $I_{\nu_0}\sim T^{5/2}$. So far it has not been tested with experimental data, but it is doubtful whether the difference is great enough to detect.

In calculating the temperature dependent spectral distribution function on the second assumption, Fowler was interested in the function for frequencies near the threshold. This allowed him to make the simplifying assumptions that the probability of excitation of any electron is independent of the frequency of the light and the energy of the electron. He then calculated the number of electrons which with the addition of the energy $h\nu$ would have sufficient energy normal to the surface to escape.

By integrating Eq. (6) for the distribution of velocities of the electrons, over all values of ξ and η one obtains the number $N(\zeta)d\zeta$ of electrons per unit volume whose z-component of velocity lies between ζ and $\zeta+d\zeta$. The number $\bar{N}$ of electrons per unit volume which can be given sufficient z-component of energy to escape, by light of frequency ν will be $N(\zeta)d\zeta$ integrated over all velocities such that $\frac{1}{2}m\zeta^2\geq h(\nu_a-\nu)$, or

$$\bar{N}=\frac{2m^3}{h^3}\int_{\xi=-\infty}^{+\infty}\int_{\eta=-\infty}^{+\infty}\int_{\frac{1}{2}m\zeta^2=h(\nu_a-\nu)}^{+\infty}\times\frac{d\xi d\eta d\zeta}{\exp\{[\frac{1}{2}m(\xi^2+\eta^2+\zeta^2)-\bar{\epsilon}]/kT\}+1}. \tag{31}$$

This integral must be expanded differently as $\mu=(h\nu-h\nu_0)/kT$ is greater or less than zero. For $\mu\leq 0$

$$\bar{N}=\frac{\pi(2m)^{3/2}}{h^3}\frac{k^2T^2}{(h\nu_a-h\nu)^{\frac{1}{2}}}\times\left[e^{\mu}-\frac{e^{2\mu}}{2^2}+\frac{e^{3\mu}}{3^2}-\cdots\right] \tag{32}$$

for $\mu\geq 0$

$$\bar{N}=\frac{\pi(2m)^{3/2}}{h^3}\frac{k^2T^2}{(h\nu_a-h\nu)^{\frac{1}{2}}}\times\left[\frac{\pi^2}{6}+\frac{1}{2}\mu^2-\left\{e^{-\mu}-\frac{e^{-2\mu}}{2^2}+\frac{e^{-3\mu}}{3^2}-\cdots\right\}\right]. \tag{33}$$

When $T\rightarrow 0$

$$\bar{N}\sim(h\nu-h\nu_0)^2/(h\nu_a-h\nu)^{\frac{1}{2}}\quad\text{for } \nu>\nu_0, \tag{34a}$$

$$\bar{N}=0\quad\text{for } \nu<\nu_0 \tag{34b}$$

when $\nu=\nu_0$

$$\bar{N}\sim T^2. \tag{35}$$

The assumption that the emission is proportional to the number of electrons with normal component of energy sufficient to escape if the entire energy $h\nu$ is added to the normal component of energy may be expressed by $I\sim\bar{N}$. Then from Eqs. (32) and (33)

$$I(h\nu_a-h\nu)^{\frac{1}{2}}/T^2=Af(\mu)=Af((h\nu-h\nu_0)/kT), \tag{36}$$

where A is a constant independent of ν and T and $f(\mu)$ represents the terms in the square brackets of Eqs. (32) and (33) as μ is greater or less than zero.

Since $\nu_a-\nu$ is large for frequencies near the threshold, small changes in ν will leave $(\nu_a-\nu)^{\frac{1}{2}}$ nearly constant, so that it can be absorbed in A. Define $\varphi(\mu)=\log f(\mu)$ and take the logarithm of Eq. (36).

$$\log(I/T^2)=B+\varphi(\mu)=B+\varphi((h\nu-h\nu_0)/kT). \tag{37}$$

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[38] L. A. Young and N. H. Frank, Phys. Rev. [2] 38, 838 (1931).

If $\varphi(\mu)$ is now plotted as a function of μ, the curve might be considered a modified spectral distribution function whose shape should be the same for all surfaces. If on the same scale, $\log I/T^2$ from experimental data be plotted against $h\nu/kT$, one should obtain a curve of the same shape but shifted parallel to itself from the theoretical one. The vertical shift necessary to bring the curves into coincidence is a measure of B, which depends on the units of current and light intensity, and the probability that a quantum of light will eject an electron. As these should be practically independent of the temperature for any one surface, the curves for the same surface at different temperatures should require the same vertical shift to bring them to the theoretical curve.

Since the theoretical curve is plotted as a function of $\mu=(h\nu-h\nu_0)/kT$ and the experimental data against $h\nu/kT$, the required horizontal shift in the curve is $h\nu_0/kT$ from which ν_0 and the work function can be calculated.

Fig. 4 shows the results of the analysis of data for outgassed palladium by the above method as reported by DuBridge and Roehr.[39] The solid line is the theoretical curve and the points represent the experimental data for the various temperatures after they have been shifted to coincide with the theoretical curve.

DuBridge[40] has pointed out that the above method requires the determination of the relative intensities of the light source for the various frequencies. He suggests that one plot $\varphi(\mu)$ against $\log|\mu|$. Then experimentally determine the emission I at various temperatures with light of a single frequency, and plot I/T^2 against $\log 1/T$ $(=-\log T)$. To make the curves coincide there will again be a vertical shift of little consequence, but the horizontal shift will be $\log(h\nu-h\nu_0)/k$ since $\log\mu=\log(h\nu-h\nu_0)/k-\log T$. Thus from the frequency ν of the incident light, ν_0 can be calculated.

To show the internal consistency of the methods and the degree to which the two methods of analyzing the data agree, the results for the emission of clean palladium are given in Table I.

TABLE I.

Fowler's method[39] Temperature of surface (°K)	Work function (volts)	DuBridge's method[40] Wave-length of incident light (A)	Work function (volts)
305	4.96	2482	4.96
400	4.97	2399	4.95
550	4.97	2378	4.94
730	4.97	2345	4.94
830	4.98	2302	4.98
925	4.98	2225	4.98
1005	4.96		
1078	4.97		
Average 4.97 volts		Average 4.96 volts	

The two methods give essentially the same result. The internal consistency of Fowler's method seems somewhat better. In either case the error in a threshold determination from the data is small compared with the error which would be introduced into the data by a small amount of contamination on the emitting surface. For a clean surface the choice of method may be governed by the convenience in obtaining the data.

Table I as well as other data[37] for clean surfaces shows no trend in threshold with temperature between room temperature and 1100°K. A trend of 1 percent or 0.05 volts in the threshold for palladium would be detected easily. The evidence is that for the metals studied, the height of the potential barrier $h\nu_a$ is constant to within 1 percent.

The vertical shift required to bring the experimental curve over Fowler's theoretical curve is B, Eq. (37), and the anti-logarithm of B is proportional to A, Eq. (36). In an experiment on one surface, A is proportional to the probability that an incident quantum will eject an electron. The reflection coefficients of most metals are sensibly constant so that considerable changes in A mean changes in the emission efficiency. Thus analysis by Fowler's method separates the changes in spectral sensitivity curves into changes in threshold and changes in emission efficiency. If B, and therefore A, varies with the temperature, Fowler's method of analysis shows this as a change in vertical shift of curves taken at different temperatures. DuBridge's method of analysis fails as a dependence of B on T will change the shape of curve as plotted, making a superposition impossible. Changes in B with impurities on the surface,

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[39] L. A. DuBridge and W. W. Roehr, Phys. Rev. [2] **39**, 99 (1932).

[40] L. A. DuBridge, Phys. Rev. [2] **39**, 108 (1932).

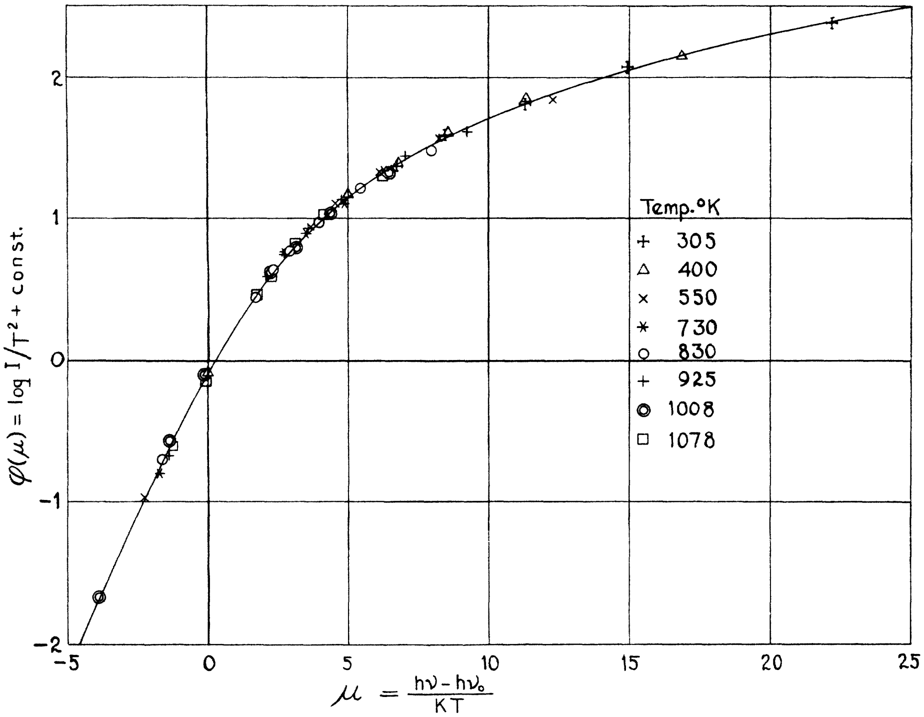

FIG. 4. Analysis of photoelectric data, for clean palladium, by Fowler's method. The points representing the data for various temperatures have been shifted to coincide with the theoretical curve. (DuBridge and Roehr.)

and with temperature are found in the data of Welch and Warner.

Welch[41] determined the spectral distribution functions for various metals at different times after renewing the surface by filing. Evidently the changes were due to gas or vapor collecting on the surface. The work functions of the metals increased with time in amounts varying up to 0.16 volts, except that for germanium which decreased slightly. Without exception the vertical shifts corresponded to decreases in the emission efficiency to about one-half.

Warner[42] used Fowler's method to analyze data for a tungsten filament. From his diagram (his Fig. 2) the change in vertical shift corresponded to an emission efficiency at 790°K about one-tenth that at 1100°K. This was ascribed to impurities on the tungsten.

In the above cases the changes in emission efficiency were large and therefore evident from the spectral distribution curves. Where the changes are small, and accompanied by changing thresholds, this method of analysis should prove of value.

For convenience in analyzing data by either method, DuBridge[40] has given a table of values of $\log_{10} |\mu|$ and of $\varphi(\mu)$ for values of μ from -8.0 to $+50.0$.

B. Saturation phenomena

As mentioned in the introduction, certain coated surfaces require abnormally high accelerating potentials in order to produce a saturation

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[41] G. B. Welch, Phys. Rev. [2] **32**, 657 (1928). Determination of work functions by Fowler's method, Phys. Rev. [2] **40**, 470 (1932). The author wishes to thank Dr. Welch for subsequently furnishing the data on the vertical shifts.

[42] A. H. Warner, Phys. Rev. [2] **38**, 1871 (1931).

current, whereas clean surfaces saturate with low fields. Ives[43] reported that it required higher accelerating fields to saturate the current from thin, than thick alkali metal films. Suhrmann[44] not only found the same effect, but also that when using light near the threshold, a higher accelerating field was required to produce saturation than when light of considerably higher frequency was used. Huxford[45] found both of these effects true for oxide coated cathodes of the type used for thermionic emitters.

This phenomenon is closely allied with deviations from Schottky's equation[46] for thermionic emission in accelerating fields, shown by activated surfaces. Schottky's equation is derived on the assumption that electrons leaving the metal surface are subject to an image field, Eq. (12), and has been verified[47, 48] for clean surfaces.

Assuming the image force law, Debye[49] showed that in an accelerating field of E e.s.-units·cm^{-1}, the effective or apparent work function ϵ_e is given by:

$$\epsilon_0-\epsilon_e=e(eE)^{\frac{1}{2}}. \qquad (38)$$

Lawrence and Linford[36] found this approximately true for shifts in threshold of a thick potassium film on tungsten. For small fields some surfaces showed greater shifts in the threshold than the theory predicts.

Deviations from Schottky's equation for thermionic emission have been investigated by Becker and Mueller[50] and by Reynolds.[51] Large deviations from Eq. (38) were found by Linford[52] on thoriated tungsten, and Huxford[45] on oxide coated surfaces.

Becker and Mueller[50] showed that if the apparent work function as a function of the field is known, the surface field against which the electrons must escape may be calculated from the formula:

$$d\epsilon_e/dE=-z_1e. \qquad (39)$$

Where E is the applied field in e.s.-units and z_1 is the distance from the surface to the point where the applied field equals the surface field, and thus to the point where the field acting on the electron is zero. The field they calculated was about the image field at distances less than 2×10^{-6} cm, but much larger at greater distances. At 10^{-4} cm the calculated field was about 1000 volts·cm^{-1} as compared to the image field of 3.6 volts·cm^{-1}.

For convenience in work with photoelectric data, Eq. (39) may be written

$$d\nu_e/dE_v=-z_1e/300h \qquad (40)$$

where ν_e is the effective threshold and E_v is the applied field in volts·cm^{-1}.

To account for lack of saturation Langmuir[53] proposed the theory that the substance on the surface formed a non-uniform film, that is, certain areas or patches were more densely covered than others. Since the work function of a film covered surface depends on the thickness of the film, some patches would have a lower work function than others. This theory has been used by various workers to explain emission data.

In order to make quantitative comparison with experimental data, it is necessary to calculate the local fields due to the patches, and then determine the emission to be expected with these fields superimposed on the image field.

If two metals A and B with work functions ϵ_A and ϵ_B, be brought in contact they will show a contact potential difference V_B-V_A. Energy considerations show that:

$$\epsilon_A-\epsilon_B=V_B-V_A+P_{AB} \qquad (41)$$

where P_{AB} is the Peltier coefficient at the junction of the two metals, and is so small compared with the other terms that it can be neglected. Thus the contact potential difference between two metals can be said to be equal to the difference in their work functions. The metal of lower work function is the more electropositive. The presence of other metals in the circuit between A and B does not affect the above relations.

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[43] H. E. Ives, Astrophys. J. **60**, 209 (1924).

[44] R. Suhrmann, Naturwiss. **16**, 336 (1928).

[45] W. S. Huxford, Phys. Rev. [2] **38**, 379 (1931).

[46] W. Schottky, Phys. Zeits. **15**, 872 (1914).

[47] S. Dushman, Rev. Mod. Phys. **2**, 381 (1930) gives an excellent review of the subject of thermionic emission.

[48] K. T. Compton and I. Langmuir, Rev. Mod. Phys. **2**, 123 (1930). The sections on contact potentials and electron emission in accelerating electric fields pp. 144–160, contain a discussion of some of these phenomena.

[49] P. Debye, Ann. d. Physik **33**, 41 (1910).

[50] J. A. Becker and D. W. Mueller, Phys. Rev. [2] **31**, 341 (1928).

[51] N. B. Reynolds, Phys. Rev. [2] **35**, 158 (1930).

[52] L. B. Linford, Phys. Rev. [2] **36**, 1100 (1930).

[53] I. Langmuir, Gen. Elec. Rev. **23**, 504 (1920).

If a surface has areas with a work function different than the rest of the surface, there will be a contact potential difference between the two classes of areas, and there will result local electrostatic fields. The contact potential of the surface as a whole may be considered only with reference to another surface at a sufficient distance that the local fields are negligible. A contact potential so determined will determine the work function of the surface in zero field. This contact potential will be the surface average of the contact potentials of the various patches.

With no accelerating field, electrons which escape through the areas of lower work function, which are the more electropositive areas, must do so against not only the image field, but also the patch field. Those escaping from the more electronegative areas travel against the image field decreased by the patch field. The potential barriers over the two types of areas are sketched in Fig. 5 for the case where the patch fields extend out from the surface to a much greater distance than the image field, and assuming equal areas of the two types of patches. The line *OB* represents the potential of field free space away from the surface, and is chosen as zero potential. The curves above *OB* are for the patches of higher, and those below for the patches of lower work function. *MN* represents the contact potential difference between the two types of patches. *MB* and *NB* represent the potentials above the centers of the respective patches, and these added to the potential of the image field *ADB* give the resulting potential barriers *AEB* and *AFB*. Above other points on the surface, the potential curves lie between these two. The height of *OB* determines the threshold in zero field, but it is evident that no electrons with just sufficient energy to escape can do so through the more electronegative patches. The effective work function of the center of the more electropositive patches in zero field is greater by an amount *OM* than their work function would be, were there no patch fields.

If an accelerating field be applied, its potential is represented by the line *OC*, Fig. 5, with a slope equal to the magnitude of the field. The resulting potential barriers (broken lines) are obtained by adding the potential of the field to those of the barriers in zero field. The change in work function is the difference in maximum heights of the barriers with and without field. The diagram shows that the effective work function of the electropositive patches (curves *AEB* and *AEC*) is decreased by an amount much greater than the effective work function of the electronegative patches (curves *AFB* and *AFC*). The work function of a clean surface with an image field barrier (curves *ADB* and *ADC*) is decreased slightly more than that of the electronegative patches. Thus in accelerating fields the effective work function of the electropositive patches determines that of the surface, and most of the thermionic electrons are emitted through these patches.

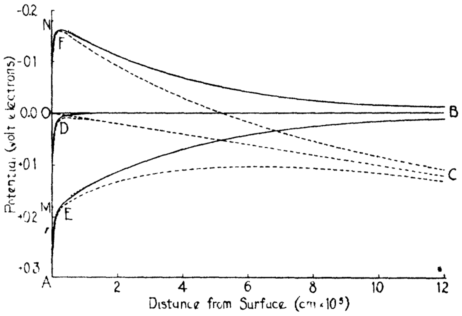

FIG. 5. Image field potential barrier as modified by patches and an accelerating field. *ADB* is the image potential. *N* and *M* are the potentials of the patches of higher and lower work functions, respectively, and the potential of the patch fields are *NB* and *MB*. The resulting potential barriers are *AFB* and *AEB*. The broken lines show the barriers in an accelerating field of 1000 volts·cm^{-1}. (Calculated for *MN* or $V_0 = 0.36$ volts and patch diameter $b = 1.8 \times 10^{-4}$ cm. See p. 50 and Fig. 6.)

For small changes in applied field, the change in maximum height of the potential barrier $\Delta\epsilon_e$, is to the first order, equal to the change in the potential of the applied field at the potential maximum. This in turn is equal to the product of the change in applied field, ΔE, the electronic charge e, and the distance z_1 from the surface to the potential maximum, or where the surface and applied fields are equal and opposite, or $\Delta\epsilon_e = z_1 e \Delta E$. This taken to the limit of small changes in field is Eq. (39).

Compton and Langmuir[48] assuming a checkerboard arrangement of patches b cm square, and such that there is a contact potential difference V_0 between adjacent patches, calculated the patch fields and expressed the result in a Fourier series. Assuming the patches to consist of clusters of closely packed thorium atoms, certain considerations led them to choose $b=10^{-6}$ cm and $V_0=1.9$ volts. The thermionic emission as a function of the accelerating field as calculated for such a surface, followed the Schottky law for low fields, and showed increasing deviations for high fields, which is exactly opposite to the observed effect. They concluded that the patch theory could not account for the observed emission.

Independently Becker and Rojansky[54] working with thermionic data and Linford[55] working with photoelectric data showed that the experimental results could be accounted for, if proper values of V_0 and b were chosen. Values of b were about 10^{-4} cm while V_0 depends on the amount of absorbed material. The assumptions as to the arrangement of patches were the same as those of Compton and Langmuir. A slight error in their expression for the potential, due to patches, V_p in the space above the surface was corrected. The corrected expression is:

$$V_p=\tfrac{1}{2}V_0+\frac{8V_0}{\pi^2}\sum_{j,k}(-1)^{j+k}\exp\left[-\{(2j+1)^2\right.$$

$$\left.+(2k+1)^2\}^{1/2}\pi z/b\right]$$

$$\times\frac{\cos(2j+1)\pi x/b}{2j+1}\cdot\frac{\cos(2k+1)\pi y/b}{2k+1}. \qquad (42)$$

$$j,\,k=0,\,1,\,2,\,\cdots$$

where the origin of coordinates is taken at the center of an electropositive patch.

The photoelectric method of determining the surface fields depends on measurements of the threshold. The place where electrons can escape with minimum energy is above the center of a patch of low work function, so the fields determined by this method will be those above the center of such patches. To calculate the field E_p above the center of an electropositive patch, set $x=y=0$ in Eq. (42), and then $E_p=-dV_p/dz$. In the correlation with the photoelectric data only the first term of the expansion was used and thus $j=k=0$. The surface field, E_s is the sum of the image field E_i and the patch field, and is given by

$$E_s=E_i+E_p=e/4z^2+(8V_0 2^{\frac{1}{2}}/\pi b)e^{-2^{\frac{1}{2}}\pi z/b}. \qquad (42a)$$

With the values of the constants $V_0=0.36$ volts and $b=1.8\times10^{-4}$ cm the observed and calculated fields were almost identical. Becker and Rojansky found that similar values of the constants gave fields whose emission characteristics were in agreement with thermionic experimental data.

Since the work function of thoriated tungsten is about 1.5 volts less than that of tungsten, the small contact potential difference between patches shows that the thorium atoms are distributed over the entire surface, and the patches are due to differences in the density of covering. The size of the patches is the same order of magnitude as the size of the tungsten crystals in the filaments used. Dr. Becker has suggested that there is a definite correlation.

The general features of the patch fields are shown in Fig. 6 where the surface fields as func-

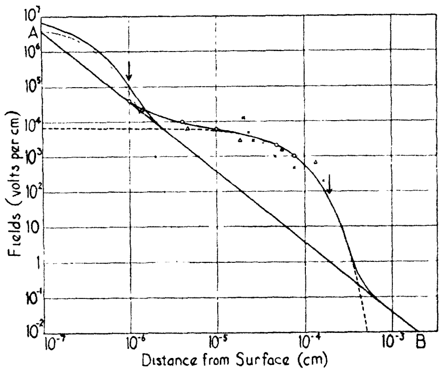

FIG. 6. Patch and surface fields plotted on logarithmic scales. AB is the image field. The broken line is the patch field for $V_0=0.36$ volts and $b=1.8\times10^{-4}$ cm. The solid line, above, which merges with AB at high and low fields is the resulting field above a patch of low work function. The circles are the photoelectrically determined fields (Linford) from which the patch constants were determined. The triangles are thermionically determined fields (Becker and Mueller), both for thoriated tungsten. The crosses are fields above an oxide cathode calculated from photoelectric data of Huxford. The dotted line and the solid line above it show the patch field and resulting surface field with the patch constants as assumed by Compton and Langmuir, $V_0=1.9$ volts and $b=10^{-6}$ cm. The arrows indicate the points on the curves where the distance from the surface is one patch diameter.

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[54] J. A. Becker and V. Rojansky in unpublished work kindly communicated to the author.

[55] L. B. Linford, Phys. Rev. [2] 37, 1018 (1931).

tions of the distance from the surface are plotted on logarithmic scales. The straight line AB is the image field. The dotted curve is the patch field calculated on the assumptions of Compton and Langmuir of $V_0=1.9$ volts and $b=10^{-6}$ cm. The solid curve above this, and merging with the image field at about 10^{-5} cm from surface, is the resulting surface field. By using the values $V_0=0.36$ volts and $b=1.8\times10^{-4}$ cm, the patch field is shown by the broken line, and the resulting surface field is the solid line merging with the image field for high fields and the patch field for lower values. In each case the arrow indicates the distance from the surface equal to one patch diameter.

The circles show the observed values of the surface field from photoelectric data[52] for which the constants were determined. The triangles show the fields for 70 percent thoriated tungsten calculated by Becker and Mueller[50] from thermionic data.

The following facts are evident from Eq. (42a) and Fig. 6: (1) That the patch field at the surface is proportional to V_0 and inversely proportional to b. (2) That out from the surface the field decreases to about one-tenth value in a distance $\frac{1}{2}b$, to one-hundredth in distance b and at $2b$ to about one-ten thousandth. The diagram shows why the values of the constants chosen by Compton and Langmuir predicted deviations from the Schottky equation at high fields.

It must be remembered that the above calculations are based on an ideal model, and the constants evaluated are therefore average values. In case the patches were not all of about the same size, but consisted of small scale fluctuations superimposed on larger patches, a two-humped curve would result which would be of the form of the uppermost solid line of Fig. 6. Actually such a case is indicated by the photoelectric data of Huxford[45] for oxide coated cathodes when calculated in terms of fields by Eq. (40). The points are indicated by the crosses, Fig. 6. Though the data does not go to high enough fields to be certain, a superposition of patches of about 10^{-5} cm diameter on patches with a diameter of 2 or 3×10^{-4} cm would account for the observed fields.

To explain the lack of saturation of the photoelectric current shown by certain surfaces at low fields, one needs only to postulate patches with b about 10^{-4} or 10^{-3} cm and V_0 of the order of a few tenths of a volt. Light near the threshold frequency can eject electrons only from the areas of lower work function. Small accelerating fields will make relatively large changes in the work function of these areas, and since the light is near the threshold frequency the relative change in the emission will be large.

If light of much higher frequency is used, emission will occur from all areas. The threshold of areas of high work function will be affected somewhat less by the applied field than would a clean surface. The relative change in emission from areas of lower work function will be less than with low frequency light, due to the fact that a given absolute change is a smaller proportion of the total emission. If the higher frequency light is in the neighborhood of the spectral maximum the absolute change in emission with apparent work function will be smaller. The net result is a much smaller relative change in total emission with applied field in light of high frequency than in light near the threshold frequency.

Extremely large changes in effective work function with applied field have been reported by Nottingham.[56] One alkali metal film on a heavy metal showed a decrease in effective work function of 1.9 volts with an accelerating potential of 4 volts. No details are given, but if plane parallel electrodes d cm apart were used, the field which caused the shift was $4/d$ volts·cm^{-1}. Reference to Eq. (39) shows that if a change of 1.9 volts in work function is produced by a $4/d$ volts·cm^{-1} field, the mean distance z_1 from the surface to where the surface and applied fields are equal must be of the order of $\frac{1}{2}d$ or about midway between the electrodes. No uniform surface charge distribution can produce surface fields at such a distance. This would indicate that there were inhomogeneities in the film with linear dimensions of the order of the distance between electrodes. These inhomogeneities might be due to a non-uniform deposition of the alkali film. While the author was working with Lawrence on thin potassium films on tungsten filaments so that patches of a size comparable with the distance between electrodes were impossible, a like effect did not exist. The sharp discontinuity in the rate

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[56] W. B. Nottingham, Phys. Rev. [2] 35, 669 (1930).

of change of the threshold with field, between that characteristic of a retarding field, and a rate about twice that predicted on image field theory, was used to determine zero field between anode and cathode.

Suhrmann and Theissing[57] reported that they found evidence for the existence of areas of widely different work function on a potassium film on platinum. They used Suhrmann's[21] method of calculating the complete emission I_c by Eq. (4) from the observed spectral distribution curves. Using Eq. (3) they plotted log I/T^2 against $1/T$. The theory predicts a straight line, of slope $-\epsilon_0/k$. They found that the slope of the curve changed with T. In the temperature range $1200°\text{K} < T < 2000°\text{K}$, where T is the temperature characteristic of the black body radiation, the slope of the curve corresponded to a work function of 2.02 volts. For the range $2400°\text{K} < T < 4000°\text{K}$ the slope indicated 2.98 volts. Their explanation was that radiation characteristic of low temperature could eject electrons only from areas of lower work function, whereas the light from a higher temperature source could eject electrons from all areas, and therefore the work function would be more characteristic of the entire surface.

Replotting the data with $r=2$, the slopes correspond more nearly to 2.46 and 2.93 volts, respectively, and with $r=5$ the plot is a good straight line. Suhrmann[22] reported that values of r higher than 2 gave better results.

An analysis of their data by Fowler's method showed that for the two thicker films, their Figs. 7 and 8, the thresholds for room and liquid air temperatures are practically the same. The very thin film, much less than 1 atomic layer, their Fig. 6, showed a work function 0.2 volts lower at liquid air temperature. Since for such films small variations in the amount of alkali produce large changes in work function, the observed difference could be the result of the condensation of a little more potassium on the surface when cooled. The shapes of all of the curves were very nearly that of Fowler's theoretical curve, which would be improbable were there large changes in effective work function with the frequency.

The curvature of the log I/T^2 *vs.* $1/T$ plots might be due to the inaccuracy of Richardson's equation as applied to photoelectric emission. The spectral distribution function that Richardson[15] calculated by equating the right-hand members of Eqs. (3) and (4) showed a steeper slope near $\nu=\nu_0$ than that observed. If the complete emission calculated from Richardson's spectral distribution function would give straight lines for the log I/T^2 *vs.* $1/T$ curves, the observed spectral distribution functions would be expected to give the shape reported by Suhrmann and Theissing even though the surface has only one work function.

Since this article was prepared, Nottingham[57a] has presented an alternate theory to account for the observed changes in the apparent work function, of certain complex surfaces, with the applied field. As previously stated these cannot be explained by the image field theory.

He presents observations of his own, and cites others, on the thermionic and photoelectric emissions of different complex surfaces, using small accelerating and retarding fields. When he studied the thermionic emission of a thoriated tungsten filament as a function of the field, he found that the observed velocity distribution was Maxwellian, but it was a distribution characteristic of a temperature higher than that of the filament. In addition, he pointed out that the A coefficient of Richardson's equation (Eq. (3)) which measures the emissivity, decreased with increasing fields. Thus with accelerating potentials of more than 6 volts, its value was of the order of one-tenth of its value for a clean surface.

To account for these phenomena, he postulated a potential barrier consisting of an image field potential similar to BDO, Fig. 2, for distances farther from the surface than the layer of thorium atoms; a potential minimum at this layer; and finally a potential maximum of approximately parabolic shape between this layer and the surface of the underlying metal. This potential maximum is postulated to be higher than AB. If the collector is at the potential of

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[57] R. Suhrmann and H. Theissing, Zeits. f. Physik **73**, 709 (1932).

[57a] W. B. Nottingham, Phys. Rev. [2] **41**, 793 (1932). The discussion of this paper has been added in proof, thus it is impossible to present diagrams which would make the explanations clearer.

AB, electrons with just sufficient energy to reach the collector would have to pass through the barrier.

If a retarding field be applied, the potential barrier out past the thorium layer would approach a line with positive slope, instead of a line like *AC*, Fig. 2, with negative slope. If the potential of the collector is higher than the top of the barrier between the film and the base metal, which will be called the "film barrier," any electron with energy enough to reach the collector will pass over the film barrier. Under these conditions the observed emission was, as it should be, the same as though no film were there. If the potential of the collector is dropped to that of the emitter, the slower electrons will have to pass through the film barrier which has a transmission coefficient less than unity. The faster electrons will still be able to travel over this barrier. This will result in the escape of a larger proportion of the high-velocity electrons, and thus the velocity distribution would be characteristic of a temperature higher than that of the filament. Nottingham was able to construct a film barrier of atomic dimensions which would produce the required filtering out of the slow electrons.

He then used this model to explain his photoelectric results previously mentioned.[56] He found that in retarding fields, the change in threshold was as predicted by the Einstein equation, (Eq. (1)); and that in moderately large fields, the shifts approached those predicted by the image field theory. With the collector near the potential of the emitter, the changes were too rapid to be explained by the image field theory, and not enough to follow Einstein's equation.

His explanation assumed that Einstein's law was followed as long as the potential of the collector remained above that of the film barrier. As soon as the collector became more negative than this, the slower electrons had to penetrate through the film barrier. Due to the fact that a finite current must flow to be measured, he pointed out that a measurable current would flow only when there were electrons excited to energies greater than the minimum required to reach the collector, after passing the film barrier. This effect would become more pronounced, the more the potential of the collector was dropped, and thus the change in the observed threshold would be less than the change in the potential of the collector.

The explanation works well so far, but fails when accelerating fields are applied. Continuing Nottingham's explanation to the region of small accelerating fields, the highest point, of the image field barrier outside the film, would be reduced according to the image law, and as before the observed change in the threshold would be less than the decrease of the image barrier. This is not what is observed, as his data, as well as all other data known to the author, show shifts equal to or greater than those predicted on the image field theory.

Nottingham's recent article shows the diagram of the photoelectric apparatus used. The emitter was a nickel cylinder inside a cylindrical collector. The former was withdrawn from the collector in order to clean and evaporate sodium onto it from the side. In preparing very thin films, it would be difficult, if not impossible, to coat the cylinder uniformily. When the films are thin, small changes in thickness mean large changes in work function. Thus patches of the order of the diameter of the emitter could be present, which as stated before would account for the effect.

The application of this theory to the thermionic effect is out of the scope of this paper, but the following observations might be interesting. It is evident that the film barrier theory will work in the region of low fields, but its application to emission in fields of the order of magnitude used by Becker and Mueller[50] is doubtful, as it would probably predict an effect similar to that predicted in the photoelectric case. This point should be investigated in greater detail.

It should also be noted that the patch theory will account for the filtering out of a part of the slower electrons emitted thermionically, and for the small value of the *A* in Richardson's equation in large fields. To do this one must remember that the patches must be subdivided into areas which have the various potential barriers between the extremes shown by *AFB* and *AEB* Fig. 5. To obtain the emission, it is necessary to calculate it for each type of barrier and sum over the surface as did Becker and Rojansky.[54] If the potential of the collector is above *F*, all areas of the surface will emit normally. If the potential of the collector is between F and B, the electropositive areas will be able to emit as before; but from the electronegative patches, only those electrons with energy sufficient to get over the barrier outside the film can escape. Thus there would be an abnormally large proportion of higher speed electrons. As the potential of the collector is dropped still more, the field becomes accelerating, then an increasing proportion of the emission comes from the centers of the more electropositive patches. This effectively reduces the emitting area of the filament and thus reduces A.

In comparing the respective merits of the two theories, one finds that the film barrier theory can explain, in a qualitative way, the photoelectric emission in very small fields, and breaks down in larger accelerating fields. The patch theory explains the phenomena in large fields, and with reasonable assumptions, explains the existing data at low fields. As will be discussed in section E, the assumption of a potential barrier, with low transmission coefficient, through which emitted electrons must pass, would lead to a small photoelectric emissivity, whereas a large one is observed for film covered surfaces. In the field of thermionics, the film barrier theory will account for observed phenomena in low fields, and the patch theory explains the emission in large accelerating fields. The possible application of the film barrier theory to emission in high fields is doubtful, whereas the patch theory can account in a qualitative way for many of the characteristics of emission in low fields. More careful experimental and theoretical investigation of this subject is needed.

C. Preparation of photoelectric surfaces

Various methods have been used to prepare photoelectric surfaces for investigation. Two methods commonly used are, evaporation in high vacuum; and for metals of high melting point, heating by radiation, conduction or electron bombardment. Two more methods have been reported recently, and the results are sufficiently good to warrant consideration.

The first method is outgassing by exposure to ultraviolet light. Millikan[58] noted an increase in photoelectric emission when metals were exposed to strong ultraviolet light. This effect has been identified as a removal of gas and has been studied by Winch[59] particularly on thin unbacked films of gold. He found that continued illumination of the gold film shifted the threshold to the red to a final value of 1.164×10^{15} sec^{-1} as compared with the value reported by Morris[60] for gold after prolonged heat treatment. Winch showed that: (1) Light of less than the threshold frequency was ineffective in outgassing. (2) The back side of the film outgassed slowly and at a relative rate comparable with the fraction of effective light transmitted through the film. (3) When the external field was reversed so that the electrons were returned to the surface the outgassing was accelerated. It appears that the photoelectrically ejected electrons knock the gas molecules from the surface.

Similar effects were noted with solid gold and a ribbon filament of silver. This method has been used by Dillon to outgas single crystal zinc.[61]

The effectiveness of electrons in removing surface gas was reported by Suhrmann,[62] who showed that electron bombardment would remove hydrogen from silver and gold which could not be removed by heating.

Rentschler, Henry and Smith[63] have reported that good photoelectric surfaces can be produced by sputtering. The metal to be investigated was prepared in wire form, it and all parts were thoroughly outgassed and then the metal sputtered from the wire onto a metal sheet to act as cathode. The work functions of tungsten and tantalum surfaces so prepared agreed with thermionic values. This method can be used for preparing surfaces of several metals which are difficult to clean by heating.

They found that thick films of certain metals

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[58] R. A. Millikan, Phys. Rev. [1] **29**, 85 (1909); [1] **30**, 287 (1910); [1] **34**, 68 (1912).

[59] R. P. Winch, Phys. Rev. [2] **38**, 321 (1931).

[60] L. W. Morris, Phys. Rev. [2] **37**, 1263 (1931), obtained a value of 1.172×10^{15} cm^{-1} for the threshold of outgassed gold.

[61] J. H. Dillon, Phys. Rev. [2] **38**, 408 (1931).

[62] R. Suhrmann, Zeits. f. Physik **33**, 63 (1925); Zeits. f. Elektrochemie **37**, 681 (1929).

[63] H. C. Rentschler, D. E. Henry and K. O. Smith, Phys. Rev. [2] **40**, 1045 (1932).

such as thorium showed higher work functions than the thermionic work function for thin films of the same metals on tungsten. This is evidently the same effect as found photoelectrically for thin alkali films. That thorium films of a certain thickness on tungsten have a thermionic work function less than thicker films has been shown by Brattain.[64]

D. Space charge effects

The possible contribution of space charge to the effective surface fields, and the resulting effect on photoelectric emission is of interest. Under conditions of high thermionic emission, space charge becomes an important factor.

Bartlett and Waterman[65] have calculated the surface fields on the assumption that space charge is the largest factor even at low emissions. In so doing they neglect the image forces which are undoubtedly present, and use Poisson's equation, which assumes continuous distribution of charge, in regions of low electron density. At low temperatures, space charge cannot be a factor in the production of fields at distances of the order of 10^{-5} cm from the surface, as will be shown in the following paragraphs, and therefore their analysis does not apply at such temperatures.

Zwickker[66] made a similar calculation, trying to work with both space charge and image effects simultaneously. It was impossible to make a rigorous solution, but from approximations, he concluded that space charge was of minor importance in the surface fields.

The effect on photoelectric emission at absolute zero can be investigated quite easily. Regardless of the source of the fields, there is a potential barrier with a height equal to the work function ϵ_0 above the energy $\bar{\epsilon}$ of the fastest electrons in the metal. Without additional energy none of the electrons can exceed the critical distance from the surface to the place where the height of the potential barrier is $\bar{\epsilon}$.* With no electrons, there will be no space charge farther from the surface than the critical distance, and thus space charge will not contribute to the potential barrier in this region. Closer to the surface the space charge may be an important factor.

Since the image law is known to hold for clean surfaces at large distances, and space charge cannot contribute in this region, the fields will be assumed to be image fields at distances greater than the critical distance. To account for observed work functions, this distance must be of the order of 10^{-7} cm, at which place the field would be about 4×10^{6} volts·cm^{-1}. The effective change in threshold in an accelerating field depends on the nature of the surface fields equal to and less than the applied field. Since experimentally applied fields are not as large as the surface fields at the place where space charge can contribute, the changes in threshold are independent of space charge.

In the limiting case of low photoelectric emission the space charge of the excited photoelectrons is small, and thus the emission characteristics observed at absolute zero would not depend on space charge.

As the temperature rises, an increasingly large number of electrons have sufficient energy to exceed the critical distance. Assuming the fields beyond the space charge region at absolute zero to be largely image fields, they should be independent of the temperature. Any contribution by space charge to the fields in this region at higher temperatures would cause an increase in the work function. Analysis of photoelectric data by Fowler's method has shown that the work function changes less than 1 percent between room temperature and 1100°K. Thus space charge is at most a minor factor in determining photoelectric emission properties in accelerating fields.

An effect reported to be due to space charge in a retarding field was found and investigated by Marx and Meyer[67] in a cell using a thick potassium film as cathode. They measured the maximum potential which the anode would attain by a string electrometer, and found that when mono-

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[64] W. H. Brattain, Phys. Rev. [2] 35, 1431 (1930).

[65] R. S. Bartlett and A. T. Waterman, Phys. Rev. [2] 37, 279 (1931). R. S. Bartlett, Phys. Rev. [2] 37, 959 (1931); [2] 38, 1566 (1931). A. T. Waterman, Phys. Rev. [2] 38, 1497 (1931).

[66] C. Zwickker, Physica 11, 161 (1931).

* Quantum mechanically there is a small probability that they will exceed this distance by a small amount, but this effect is negligible.

[67] E. Marx, Naturwiss. 17, 806 (1929); Phys. Rev. [2] 35, 1059 (1930); A. E. H. Meyer, Ann. d. Physik 9, 787 (1931); and a theoretical discussion, E. Marx and A. E. H. Meyer, Phys. Zeits. 32, 153 (1931).

chromatic light was used, Einstein's relation, Eq. (1), was satisfied. If light of high frequency be used the anode will reach a definite potential, and if light of lower frequency but still above the threshold frequency be added, the anode potential will drop an amount proportional to $(\nu_1-\nu_2)$ $n_2\nu_1/n_1\nu_2$ where ν_1 and ν_2 are the two frequencies such that $\nu_1>\nu_2>\nu_0$ and n_1 and n_2 are the numbers of electrons ejected by the light of frequency ν_1 and ν_2 respectively.

The theoretical explanation given is based on the change in the distribution of space charge between the electrodes due to the addition of the light of lower frequency, resulting in an increase in the energy required to eject an electron from the cathode with energy sufficient to reach the anode. This decrease in maximum potential was found to depend on the ratio n_2/n_1 and not on the absolute magnitude of either. When considered for low light intensities, the electron density between the electrodes would be so small that Poisson s equation used in the treatment would not apply because of the corpuscular nature rather than continuous distribution of electric charge. Since the experimental facts can be explained in a simpler manner, further theoretical discussion seems unnecessary.

Following the first published note which gave no experimental details, Olpin[68] proposed the following explanation. The equilibrium potential in monochromatic light would be reached when the number of electrons with energy sufficient to reach the anode equaled the number released from the anode by scattered light. With potassium in the cell there would be a thin film on the anode which would make it photoelectrically sensitive, and probably more sensitive than the cathode. If light of lower frequency be added no additional electrons can reach the anode, but the scattered light of lower frequency will release electrons from the anode, and its potential must drop until the necessary additional number of electrons ejected from the cathode by the higher frequency light can reach the anode. Olpin could not obtain the effect using a photoelectrically insensitive anode.

The complete report of the experimental work of Marx and Meyer showed that they had completely shielded the anode from scattered light and thus thought they had eliminated the possibility of an effect due to scattered light. Since they had potassium in the cell, a photoelectrically sensitive film would be deposited over all the glass surfaces. These would act exactly as the anode in Olpin's explanation. Photoelectrons ejected from the cathode could not reach the anode unless the surrounding glass were at as high a potential as the anode, and thus the entire inside of the tube would act effectively as would the anode were it exposed. Thus Olpin's explanation of the effect with the above extension appears to be sufficient.

E. The spectral selective effect of composite surfaces

Fowler[69] proposed an explanation for the positions of the spectral selective maxima shown by composite surfaces. These surfaces are characterized by both an electropositive substance and a dielectric on the surface. He assumed that the potential barrier of such a surface might be idealized as in Fig. 7, having two maxima with a minimum or valley between. If an electron with energy ϵ strikes the surface from within, its probability of transmission through the barrier is greater if its classical kinetic energy $\epsilon-\epsilon_2$ in the potential valley is such that the corresponding de Broglie wave-length will resonate in the width of the valley l_2. Fowler calculated the condition for resonance to be:

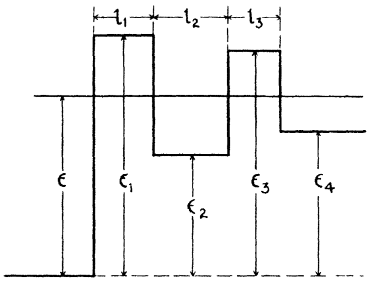

FIG. 7. Potential barrier assumed for selective transmission. (Fowler.)

$$\epsilon-\epsilon_2=n^2h^2/8ml_2^2; \qquad n=1, 2, \cdots. \tag{43}$$

He showed that for $n=1$ and a reasonable width

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[68] A. R. Olpin, Phys. Rev. [2] **35**, 112 (1930).

[69] R. H. Fowler, Proc. Roy. Soc. **A128**, 123 (1930).

of the potential valley a selective transmission would be predicted in the visible.

Olpin[70] has tried to test quantitatively the theory and has used many complex surfaces, some of which definitely showed evidence of small crystals formed on the surface, and others were noncrystalline. For those surfaces which showed crystal formation he calculated the distance between alkali atoms along lines which passed as far as possible from the electronegative atoms of the dielectric substance. Electrons in escaping would select such paths since the potential barriers would be lowest.

From the experimentally observed frequencies producing the selective maxima, and tacitly assuming that the kinetic energy of the electron in the potential valley be equal to the energy of the incident light quantum, he calculated the width of the valley which would cause the electrons to be transmitted selectively.

For the various alkali hydrides the ratios of the widths of the valley so calculated to the distance between successive alkali atoms along the chosen path varied from 0.98 to 1.01. The alkali oxide and sulphide surfaces and others were more complicated since different compounds with different crystal structures can be formed. The various crystal structures shown by any two substances, e.g., caesium and oxygen, gave spacings which were correlated with the different selective maxima shown under different conditions by cells containing these elements. The numerical agreements were close in all cases.

In this application of Fowler's theory to complex surfaces the exact numerical agreements would not be expected for the following reasons. Olpin mentioned the first one in his report.

(1) The width of the valley was correlated with the distance between the successive potential maxima. To be correct this latter distance must be reduced by the width of the potential barrier at the potential corresponding to the energy of the electron. In the case of the hydrides there was no secondary rise of the spectral distribution curve for electron energies a volt above the selective energy. Since the transmission coefficient is practically unity for electrons with energy sufficient to escape over all barriers, the barriers must be a volt higher than energy of electrons which can be transmitted selectively, to prevent a secondary rise of the spectral distribution curve within a volt of the selective maximum. From the potential curve along the path of emission shown by Olpin, an electron with energy a volt less than the maximum of the potential barrier would be in the barrier for a considerable portion of the distance, and the width of the valley would be less than assumed. In general this would apply to all surfaces.

(2) The kinetic energy of the electron was assumed to be that of the incident light quantum. This could be true only if the energy of the electron before excitation was equal to the potential at the bottom of the valley.

(3) Fowler obtained Eq. (43) from the following relation by neglecting δ

$$(\epsilon-\epsilon_2)^{\frac{1}{2}}\mu l_2=n\pi+\delta; \qquad n=1,\,2,\,\cdots; \qquad \mu^2=8\pi^2 m/h^2. \tag{44}$$

In the case of the hydrides, the heights of various parts of the potential curve can be estimated, and the value of δ may be as large as $\pi/3$. Since the value $n=1$ was used, neglecting δ could cause a numerical error as large as a factor of 5/3 in Eq. (43).

It is difficult to understand how the above mentioned corrections could compensate to give the reported numerical agreements for such a wide variety of surfaces.

Zachariasen[71] quoted recently determined crystal constants for the hydrides from x-ray data, and stated that the new values destroyed the correlation reported by Olpin. With the exception of Li H, the newer values are 1.08 to 1.10 times the older ones, thus reducing the correction necessary for the part of the electron path which is in the barrier, making the correlation more probable.

There is a general difficulty in applying Fowler's theory to the complex surfaces. A prominent characteristic is their high emission per unit light intensity. Films of pure alkali metals which have thresholds and spectral maxima in about the same regions as do certain complex surfaces have much lower emission efficiencies. For such surfaces the transmission coefficient is practically unity. Fowler's theory as applied to complex

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[70] A. R. Olpin, Phys. Rev. [2] **38**, 1745 (1931).

[71] W. H. Zachariasen, Phys. Rev. [2] **38**, 2290 (1931).

surfaces requires the electrons to travel through several potential barriers of considerable magnitude, and even with selective transmission it would not be expected to be unity.

A theory which would account for the selective maximum by means of a selective absorption of light by electrons which may be ejected would overcome this difficulty. Two possibilities are suggested by the work of Tamm and Schubin.[30]

They emphasized the fact that electrons could be excited only when in an electric field, and that the greater part of the electrons ejected from a clean surface by light near the threshold frequency were in the region of the surface fields when excited. At the same time only a small part of the light is absorbed at the surface where the efficiency of emission is high. Most of the light is absorbed by low energy electrons, in the interior of the metal and these cannot escape.

The theory predicts a definite maximum for the surface effect, and its position in relation to the threshold is not far different than that observed for the hydrides using the value of $\bar{\nu}$ for the alkali itself as an approximation. Where no definite crystalline structure is formed on the surface, the fields between the atoms or groups of atoms of the two different kinds, would be more of the order of the surface fields. The thickness of such composite films is great enough to absorb a considerable proportion of the incident light and this in a region where surface type excitation with its high efficiency might occur.

With a crystalline structure in the complex surface there would be periodic fields in the crystal, which like the lattice fields in the interior of the metal would give rise to definite energy levels of the electrons. These energy levels would depend on the structure and constants of the crystals. The volume effect for such crystals might account for some of the maxima. On such a theory electrons would not need to pass through potential barriers, with the resulting lower transmission coefficient.

More detailed study as to the structure of the complex surfaces and the theory of photoelectric excitation of electrons in such surfaces is needed in order to explain satisfactorily their extreme sensitivities as well as the positions of their spectral selective maxima.

F. The vectorial effect

Recent work of Ives[72] and Ives and Briggs[73] has explained the dependence of the emission from thin alkali films deposited on heavy metals on the angle of incidence and the polarization of the light and on the optical constants of the two metals. They have been able to correlate the emission with the energy density of radiation in the alkali film.

Wiener's work has shown that the interference of incident and reflected light waves produces standing waves above a surface of discontinuity. A node in the standing wave system would be found at the surface of a perfect electrical conductor.

Since metals have finite conductivities, the nodes are displaced, giving finite values of the electric vectors of the light at their surfaces. From the work of Fry,[74] the magnitude and direction of the electric vector at the surface can be calculated from the optical constants of the metal, and the angle of incidence θ and the polarization of the incident light.

The energy density at the surface is proportional to the square of the magnitude of the electric vector, or its intensity. Since the area of the cathode covered by a defined beam of light is proportional to sec θ, the electric intensity must be multiplied by this factor before comparison with experimental data. In the subsequent discussion of comparisons with experiments, the electric intensities will be assumed to have been multiplied by sec θ whether specifically so stated or not.

The experimental work was done on alkali metal films reported to be about one atom thick. From their emission characteristics and comparison with Brady's results,[14] it is probable that they were thicker, but less than 10 atomic layers. This change would not affect the validity of Ives' conclusions. The films investigated were not visible on the surface, and thus one can assume that they do not affect appreciably the optical constants of the underlying metal. The thickness of the film at most is a small part of a wave-length

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[72] H. E. Ives, Phys. Rev. [2] **38**, 1209 (1931).

[73] H. E. Ives and H. B. Briggs, Phys. Rev. [2] **38**, 1477 (1931).

[74] T. C. Fry, J. Opt. Soc. Am. **15**, 137 (1927); **16**, 1 (1928).

of light, and therefore the electric vector at the surface of the alkali film can be assumed to be that at the surface of the underlying metal.

When light enters the alkali film the components of the electric vector parallel to the surface are continuous, but the component normal to the surface must be multiplied by the factor $Q=(N+iK_0)^{-2}$, which depends on N the index of refraction and K_0 the extinction coefficient of the alkali metal.

For notation the electric vector of the standing wave at the surface of the metal will be denoted by $E_{||}$ if the incident light is polarized parallel to the plane of incidence, $E_{\perp}$ if polarized perpendicular to this plane, and $E_{\underline{\perp}}$ if the light is incident normal to the surface. The two latter quantities will be the same in the alkali film, but the former will be different. To calculate $E_{||}'$ the electric vector in the alkali film for parallel polarized light, the component of the electric vector normal to the surface outside must be multiplied by Q before obtaining the resultant.

Ives[72] worked with a potassium film on platinum and measured the photoelectric emission for both polarizations as a function of the angle of incidence. Fig. 8 shows the data for light of 5461A. The solid lines show the calculated values of the electric intensities at the surface of the platinum for both polarizations, $|E_{||}|^2$ and $|E_{\perp}|^2$. The broken line shows the intensity calculated for the interior of the potassium film, $|E_{||}'|^2$. The experimental data are shown by the circles and crosses. At 4359A, the data for the observed emission fell on a curve above that for $|E_{||}|^2$. The optical constants for potassium are not known for this spectral region, but extrapolations show that $|Q|>1$, thus qualitatively satisfying the data.

A similar comparison of experimental and calculated data for rubidium on glass showed good agreement.

To demonstrate the importance of the optical constants of the underlying metal, Ives and Briggs[73] investigated thin films of sodium on silver. Sodium was chosen because the films were more stable due to its lower vapor pressure. Investigation of sodium films on platinum showed no sudden changes in emission with the frequency, and since the optical constants of platinum show no large variations over the frequency range studied, it was evident that those of sodium have no abrupt changes.

Silver was chosen as the underlying metal because it has a transmission band at 3160A, and its optical constants show widely different values in the three spectral regions, defined roughly as near 3160A, at longer, and at shorter wavelengths. In this way the emission from one alkali film can be studied as the optical constants of the underlying metal are changed by changing the wave-length of the incident light.

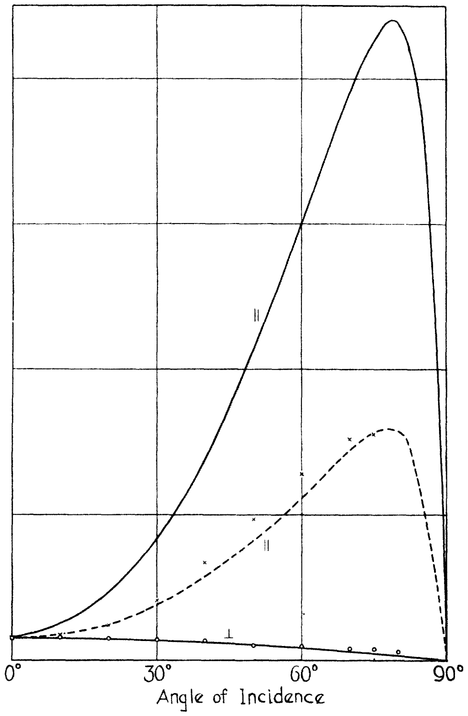

FIG. 8. Comparison of calculated intensity of electric vector with photoelectric emission, for various angles of incidence. The solid lines show the electric intensity above surface of platinum for both polarizations, and the broken line shows the intensity in the potassium film. The photoelectric data are the circles and crosses. Wave-length of light 5461A. (Ives.)

The electric intensities at the surface of the silver as calculated for the frequency range studied, for light of normal incidence, and for both polarizations at 60° incidence showed several interesting characteristics.

At 3260A or 100A longer wave-length, than the transmission band $|E_{||}|^2$ shows a sharp minimum and $|E_{\perp}|^2$ a maximum. $|E_{\underline{\perp}}|^2$ has a definite maximum at about 3300A. The emission curves show these same characteristics. That the emission cannot be correlated with the reflecting power of silver is shown by the fact that similar curves for the reflecting power all show minima between 3100A and 3200A.

Between about 3100A and 3300A the curve for $|E_{\perp}|^2$ is higher than that for $|E_{\underline{\perp}}|^2$ which predicts that for this range the emission due to perpendicularly polarized light at 60° incidence should be greater than that at normal incidence. At other wave-lengths it should be less. If an effect of this kind exists, curves of emission as a function of angle of incidence for perpendicular polarization would show a maximum, instead of a monotonic decrease from 0° to 90° incidence as shown in Fig. 8. Such angle curves were taken at intervals from 3022A to 3650A. Curves for wave-lengths greater than 3300A showed no maximum, the others did. At the shortest wave-lengths investigated the maximum became less pronounced, and at 3022A the emission at 60° was the same as at normal incidence. Experimental difficulties made investigation at shorter wave-lengths impractical.

Thus the emission from thin alkali films follows the changes in intensity of the electric vector in the film as calculated from the optical constants of the underlying metal and of the film. In this way the vectorial selective effect of such films is explained completely without the assumption of a greater efficiency of emission for the component of the electric vector of the light normal to the surface, than for the components parallel to the surface.

Fleischmann[75] has found that thin potassium films on glass show an absorption band in the visible if the incident light not at normal incidence is polarized parallel to the plane of incidence and no absorption if polarized prependicular to this plane. He correlates this with the vectorial effect. From the work of Ives and Briggs it would appear that the absorption of light as well as the photoelectric emission depends on the intensity of the electric vector in the alkali film.

Ives and Briggs[76] investigated the emission properties of sodium films, during their formation on silver, with light of frequency near the transmission band of silver at 3160A. In their previous work[73] they had studied the emission from comparatively thick films, and found that the emission characteristics could be correlated with the intensity of the electric vector above the surface of the silver. They concluded that the photoelectrons originated in the alkali films.

In the more recent work, they found that film free silver was photoelectrically insensitive to light of this frequency; and that when a little alkali (much less than enough to form a layer one atom deep) was allowed to deposit on the silver, it emitted photoelectrons. As before, these films were studied with light incident normal to the surface, and with both polarizations with the light incident at 60°. The emission characteristics found were unlike those of the thick film, but they could be correlated very well with the absorbing power of the layer of silver just inside the surface. Thus it would appear that most of the photoelectrons originated in the surface layer of the silver.

By studying the films as their thicknesses increased, it was found that the emission characteristics changed gradually to those found for a thick film, indicating that as the film became thicker, an increasing proportion of the photoelectrons originated in the alkali film. This work gives very good evidence that a large proportion of the photoelectrons have their origin very close to the surface of the emitter.

The experimental extension of this work to the bulk alkali metals will depend on the determination of their optical constants. It seems reasonable that the relations found to hold so well for thin films should be true in general. If so, this work gives the foundation for better general theories of the photoelectric effect. It points out that the magnitude of the electric vector at the surface as calculated from the standing wave pattern is an important factor in the emission,

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[75] R. Fleischmann, Naturwiss. 19, 826 (1931).

[76] H. E. Ives and H. B. Briggs, Phys. Rev. [2] 40, 802 (1932).

and the theories should be modified to include this.

The fact that the emission depends on the intensity and not on the orientation of the electric vector at the surface is in disagreement with all the quantum mechanical theories, which predict much greater efficiency for the component normal to the surface. This cannot be explained by collisions of the electrons with the lattice before leaving the surface, as on this assumption Fowler obtained a wrong result for the temperature correction.

Momentum considerations may play an important part in determining the direction of the increase in velocity of the electron when it absorbs a quantum. The change in momentum of the electron is of the order of 10^4 times the momentum of the incident quantum. This extra momentum must be transferred by means of the electrostatic field to the lattice ions. If, as Tamm and Schubin[30] point out, the emission for frequencies near the threshold is principally from the region where the surface fields are large, and since these fields are unidirectional the change in momentum of the electron must likewise be unidirectional. How much the probability of excitation of the electron depends on momentum considerations and how much on the direction of the electric vector should be investigated in greater detail.

Although the recent theories and experiments have done much to unify and explain many of the photoelectric phenomena, there is still a great amount of careful and well directed experimental work to be done, which must be coupled with more detailed theoretical investigations, in order to produce a satisfactory unified picture of the photoelectric effect.

In conclusion the author wishes to thank Professor E. U. Condon for suggesting the preparation of this article and for his continued help; Doctors J. A. Becker, V. Rojansky, A. R. Olpin and W. H. Brattain for their helpful suggestions and criticisms during the preparation of this paper. The author also wishes to express his appreciation to the National Research Council and the Palmer Physical Laboratory for making this study possible.