THE EFFECT OF INTENSE ELECTRIC FIELDS ON THE PHOTOELECTRIC PROPERTIES OF METALS

By Ernest O. Lawrence and Leon B. Linford
University of California

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Abstract

The photoelectric effect from thin films of potassium and oxygen on tungsten has been studied as a function of strong accelerating fields. Fields as high as 63,000 volts/cm were used which shifted photoelectric thresholds towards the red, the shifts being approximately proportional to the square root of the applied fields. An applied field of 36,000 volts/cm removed the threshold for a pure potassium layer on tungsten from 5620A to 5880A. A film of potassium on a very thick layer of oxygen on tungsten showed a threshold at 6800A which did not vary with applied accelerating fields. However the magnitude of the emission increased with the field suggesting that thick oxygen layers are rough and applied fields over most of such surfaces are much smaller than calculated from the geometry of the electrodes. A layer of potassium on a thin layer of oxygen on tungsten showed a threshold at 7350A for small applied fields which shifted to 7575A for a field of 18,600 volts/cm. A film of potassium on a thinner layer of oxygen—perhaps less than a monatomic layer—exhibited a threshold in small fields at 5830A which was shifted to 5960A by an applied field of 18,600 volts/cm. From the observations of the variations of the shifts with applied fields calculations of the surface fields were made after the manner of Becker and Mueller. It was found that outside the film of potassium on a thin layer of oxygen on tungsten the field followed closely the Schottky image law in the range 1.5×10^{-6} cm to 10^{-5} cm from the surface. The pure potassium film on tungsten exhibited surface fields which were closely image fields between 8×10^{-7} cm and 1.5×10^{-6} cm from the surface but which departed from the image law at greater distances. These observed departures were about equal to the image fields and were much smaller than the surface fields at like distances outside thoriated tungsten filaments as recorded by the thermionic measurements of several observers. The surface fields in excess of the image fields are ascribable to inhomogeneity of the surfaces, regions of different work functions having linear dimensions of the order of magnitude of 10^{-5} cm.

Shifts of photoelectric thresholds by strong accelerating fields are of particular theoretical interest for they involve changes of the work function of a surface without alterations of the other important characteristics of the metal. It is found that the form of the photoelectric sensitivity versus frequency curve remains unchanged over the range of observations and shifts along with the thresholds in intense fields. Thresholds are not sharp but approach the frequency axis tangentially. These observations are in excellent agreement with the theory of the photoelectric effect based on wave mechanics and the Fermi-Dirac distribution of the electrons in metals worked out by Wentzel and modified by Houston.

THE new quantum mechanics in the hands of Pauli, Sommerfeld, Wentzel, Fowler, Houston, Nordheim and others[1] has been highly successful in dealing with many general properties of metals, and has given a particularly satisfactory account of the emission of electrons from metal surfaces.

[1] An excellent résumé of the subject by L. Nordheim is to be found in Phys. Zeits. **30**, 177 (1929).

The old concept of free electrons in metals has been revived, though to be sure the behavior of these electrons on the present theory differs radically from that of former views. For purposes of discussion of the experimental results herein described it is desirable to emphasize two characteristic features of the new theory.

The first has to do with the work function of a metal surface. The constant b in Richardson's thermionic equation and the photoelectric long wavelength limit have been regarded as measures of the minimum amount of energy given to an electron in the process of its ejection from a metal. On the older theory the free electrons possessed a Maxwellian distribution of velocities and were retained in the metal by a potential difference between outside and inside equal to the work function. The newer theory attributes a Fermi-Dirac distribution of velocities to the electrons and assigns a potential energy barrier at the surface which exceeds the maximum energy of the electrons at the absolute zero of temperature by the amount of the work function. The work function involves more than just the work required to eject an electron from inside to immediately outside a metal, for it includes as well the work required to remove it entirely away from the surface. Outside the metal an electron experiences a force of attraction to the metal produced by its image. In some cases inhomogenous ion layers also produce electrostatic fields near metal surfaces which aid or oppose the removal of electrons.

It is obviously possible to introduce electric fields at metal surfaces which reduce the image and ion fields, and thereby cause reductions of the work function. Such reductions of the work function in strong fields have been observed by workers in the field of thermionics, and indeed variations of the thermionic emission with applied fields have been used to estimate surface electric fields.

The second feature of the new theory is that it yields a definite probability that an electron will pass into a region in which its classically computed potential energy is greater than its total energy before entering the region. The probability of finding an electron in such a region falls off exponentially with the distance into the region. This feature of the theory is one aspect of the wave nature of matter. It is possible to apply such a strong electric field at the surface of a metal that the potential within a few atom diameters of the surface becomes lower than the energy of some of the electrons within the metal. Any electron, which passes into this region of higher potential far enough to reach the point where the applied field has lowered the potential to that corresponding to the energy of the electron in the metal, will be accelerated away from the surface. This effect, which is analogous to the passage of light unaffected from one glass plate into another when the plates are close enough together, satisfactorily explains the observed emission of electrons in strong fields.

These effects of strong accelerating fields on the emission of electrons from metals, also should be clearly displayed by a dependence of photoelectric emission on such fields. The lowering of the work function by fields

should appear as a shift of the photoelectric threshold to the red, as has been pointed out by Becker and Mueller.[2] Similarly the ability of electrons to go through high potential barriers should be evidenced in a like manner. That effects of this sort exist, has been indicated by the observation of Ives[3] who found difficulty in saturating photoelectric currents from thin alkali metal films, while currents from thicker ones were more easily saturated. Suhrmann[4] also noted this lack of saturation, and its variation with the thickness of the film, and noted the further effect that the saturation becomes the more difficult the nearer the frequency of the incident light approaches the threshold value. The reports were only qualitative, and no mention was made of a possible shift in the threshold frequency being associated with the phenomena.[5]

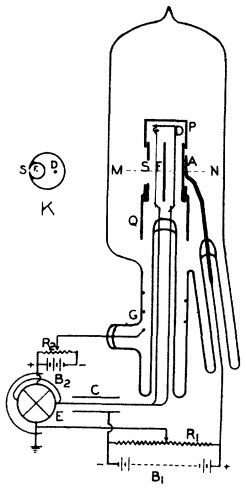

Fig. 1. Diagram of apparatus, showing a section through the photoelectric cell with a schematic diagram of the electrical connections. Also K a cross-section through the anode A along the line MN.

The present work was designed to investigate the matter in a quantitative manner with the primary view of verifying the predictions of the newer theories and also to use the experimental data to elicit information on the surface electrostatic forces near various metal surfaces.

Apparatus and Experimental Methods

Figure 1 shows a section through the photoelectric cell and a schematic diagram of the electrical connections. K is a cross section through the anode A on the line MN. The anode was made from a solid block of nickel in the

[2] J. A. Becker and D. W. Mueller, Phys. Rev. **31,** 431 (1928).

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

[4] R. Suhrmann, Naturwissenschaften **16,** 336 (1928).

[5] Nottingham (abstract Feb. meeting Am. Phys. Soc.) has recently observed interesting shifts of photoelectric thresholds produced by very small applied fields.

form of two internally tangent cylinders. In their common wall was a 1 mm slit S, 1 cm long, to allow the light to fall on the tungsten filament F stretched along the axis of the inner cylinder. The filament was held in place by the nickel support D passing through the crescent shaped space between the two cylinders. The screw on cap P and the sliding sleeve Q were so arranged, that when in place they screened all parts of the cathode circuit, inside the tube, from light and external electrical effects. Both filament leads were carried out of the tube so that the filament could be glowed.

The tube was baked out under vacuum for 12 hours at a temperature of 500° C, the metal parts were heated with an induction furnace and the filament glowed at about 2200° C. The potassium was then distilled into the tube after repeated distillations, and the tube was sealed off when the pressure was less than 10^{-6} cm of Hg. To obtain a coating of oxygen on the filament, a little air was allowed into the tube, after baking out and before distilling the potassium, and then pumped out immediately.

Light from a 6 volt, 110 watt ribbon filament lamp, was dispersed by a Van Cittert type double monochromator, which gave light bands about 100 cm^{-1} units wide (corresponding to a width of 32A at 5600A) which were practically free from stray light. Any desired band of the visible spectrum could be selected by moving the middle slit. This made it unnecessary to change the adjustment of the last slit or of the photoelectric cell when measuring the current for various wave-lengths.

The photoelectric current was measured with a quadrant electrometer E using the accumulation of charge method. To prevent leakage of charge from the anode circuit to the electrometer circuit, a guard ring G consisting of several turns of tungsten wire was placed in the stem carrying the filament leads. Metal foil, used as a screen on the outside of the tube, was also connected to the guard ring circuit. A low voltage battery B_2 and potentiometer R_2 were used to balance out the effects of contact potentials.

The accelerating fields were produced by potentials from a 1500 volt bank of storage "B" batteries B_1. These were connected across a resistance R_1 of about 5×10^5 ohms. Only a part of the battery potential was applied between the anode and the electrometer case. The remainder was used to produce a negative potential on the compensating condenser C. The ratio of the potentials on the anode and compensating condenser was so adjusted that the electrometer system was rendered immune to fluctuations in the voltage of the batteries.

The data are shown by plotting the sensitivity curves, that is the photoelectric current per unit light intensity against the frequency of the incident light in sec^{-1} units. The absolute values of the light intensity and of the photoelectric current were not determined. The maximum current was of the order of 10^{-14} amps.

The relative intensities of the light of the various wave-lengths were determined by a vacuum thermopile set in the place of the photoelectric cell.

The accelerating fields were calculated from the applied potentials and

the dimensions of the cylinder and filament. The inside diameter of the nickel cylinder was 0.228″ or 0.579 cm. The field at the surface of the filament in the cell with a filament 0.9 mil (0.0023 cm) in diameter was $E=160V$; and at the surface of the filament 3.0 mil (0.0076 cm) in diameter, $E=60.4\ V$, where V is the applied voltage.

The small diameters of the filaments together with the fact that only about 0.7 cm of the filament was illuminated explain the small values of the photoelectric currents.

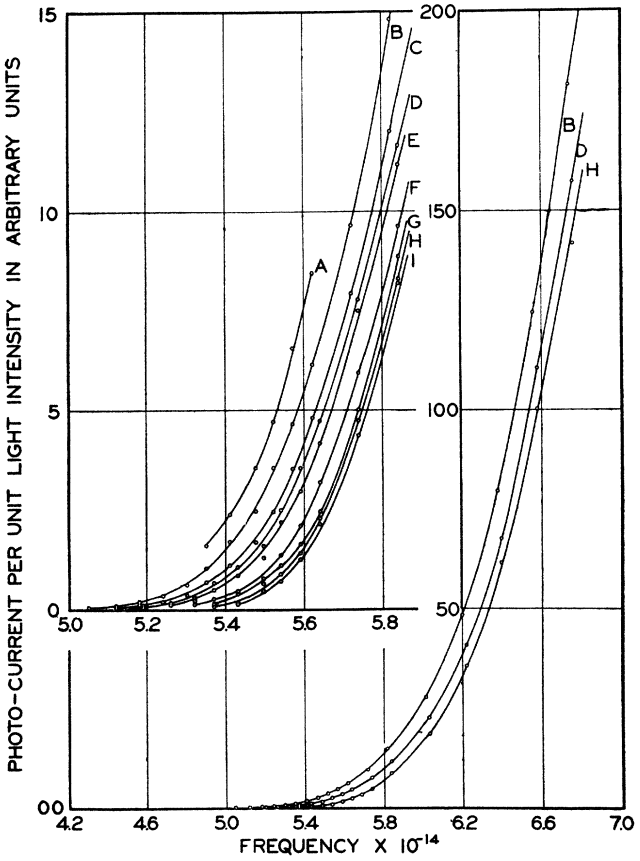

Fig. 2. The photoelectric current as a function of the frequency of the incident light for a potassium film on tungsten for various fields drawing electrons away from the surface. At right, complete curves for three values of the field. At left, similar curves for nine values of the field on an enlarged scale. The fields in volts per centimeter are for the curves A to I: A, 63, 100; B, 36,200; C, 22,100; D, 15,800; E, 9000; F, 3100; G, 1000 H, 260; and I, 0.

Experimental Results

The photoelectric sensitivity curves for a film of potassium on the 0.9 mil tungsten filament, for different voltages are shown in Fig. 2. The three curves to the right are the sensitivity curves over the range of wave-lengths studied. The photoelectric threshold with an accelerating field of 260 volts/

cm, curve *H*, was 5620A (5.35×10^{14} sec^{-1}) and for fields of 36,200 volts/cm, curve *B*, the threshold was shifted to 5880A (5.10×10^{14} sec^{-1}).

At the left, the portions of the curves near the threshold are plotted on an enlarged scale. The scale of frequencies has been doubled and that of the current increased tenfold. The increased scale allows the current taken with

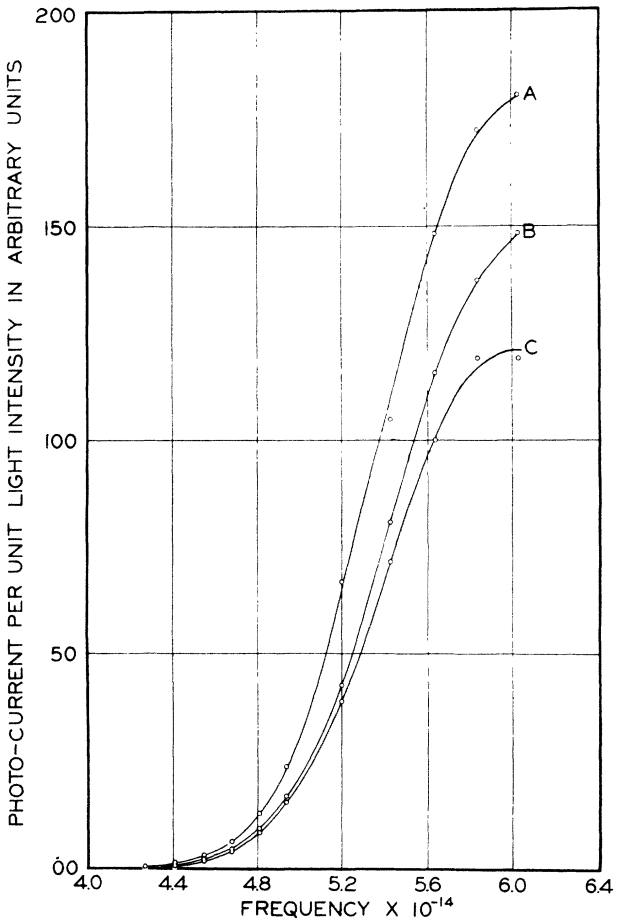

Fig. 3. The photoelectric current as a function of the frequency of the incident light for potassium on a thick layer of oxygen on tungsten. The fields in volts per centimeter for the curves *A* to *C*: *A*, 18,300; *B*, 4570; and *C*, 366.

the nine different accelerating fields to be plotted, while at the right only three representative ones have been selected. The fields for curves *A* to *I* in volts per centimeter are: *A*, 63,100; *B*, 36,200; *C*, 22,100; *D*, 15,800; *E*, 9000; *F*, 3100; *G*, 1000; *H*, 260; and *I*, 0. It was not possible to use higher electric fields, because of the setting in of field currents of the same order of magnitude as the photoelectric currents. *It is evident from the figure that the shift is not proportional to the strength of the field, but as will be shown later,*

is more nearly proportional to the square root of the field. Not only is the threshold shifted, but the entire sensitivity curve is displaced by the field. The curves do not meet the frequency axis at a finite angle, but approach tangentially, as near as can be experimentally determined. The recorded thresholds were arbitrarily chosen as the points where the currents became definitely measurable.

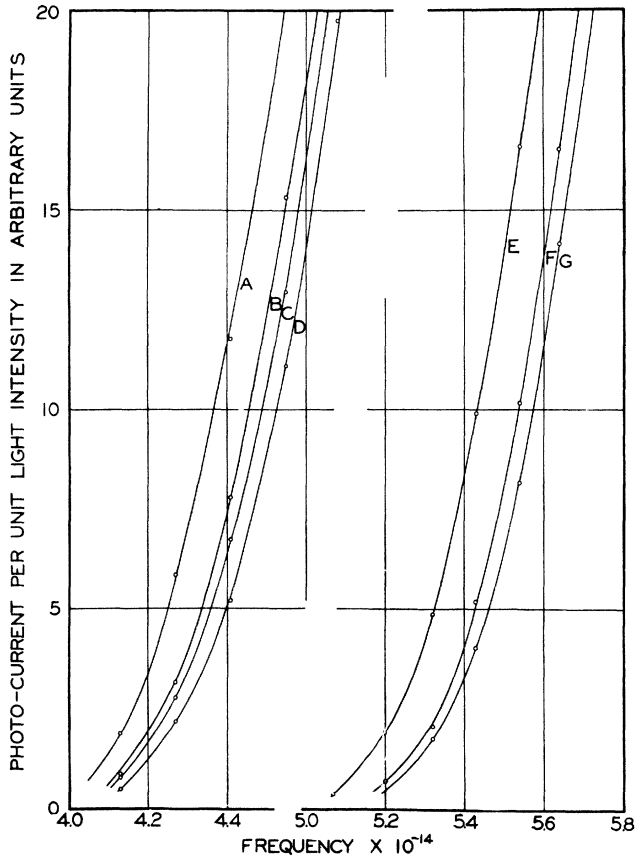

Fig. 4. The photoelectric current as a function of the frequency of the incident light. Curves *A* and *D* for the surface of figure 3 after being heated to 1100° C. The fields in volts per centimeter are: *A*, 18,600; *B*, 4650; *C*, 372; *D*, 0. Curves *E* to *G* show data obtained from the same surface after being heated to 1600° C. The fields are: *E*, 18,600; *F*, 372; and *G*, 0.

To test for the existence of contact potentials between the filament and anode, a photoelectric sensitivity curve was made with a retarding potential of 0.7 volts. The curve cut the frequency axis where the frequency was 1.3×10^{14} greater than for zero potential. This corresponds to a shift of 0.54 volts. Thus the contact difference in potential was less than 0.2 volt in a direction to produce an accelerating field.

A layer of oxygen was allowed on the 3.0 mil filament before the potassium was distilled into the tube. The results shown in Fig. 3 show that the thres-

hold of this surface was not appreciably shifted by fields as large as 18,300 volts/cm. Near the maximum sensitivity, the emission with a field of 18,300 volts/cm was 1.5 times, and at 4570 volts/cm was 1.17 times the emission at 366 volts/cm (curves *A*, *B* and *C* respectively). The oxygen layer shifted the threshold from 5620A for the pure potassium surface to 7100A (4.25×10^{14} sec^{-1}). At the same time the nature of the surface was changed so that the threshold was little affected by the accelerating fields.

The filament was then heat treated at about 600° C for 5 minutes, allowed to cool and observations were made. It was then heat treated at successively higher temperatures up to about 1600° C. Curves *A* to *D*, Fig. 4, show the emission from the filament after being heated to 1100° C and then allowing the potassium to distil back onto the filament with the reduced oxide coating. Heat treating at this temperature produced the first observable difference from the unheated surface. Curves *E* to *G* show the results after the filament had been heated for a few minutes at 1600° C. These curves show only the region near the threshold on the enlarged scale used for the left half of Fig. 2. They are not continued to the frequency axis because when taking the data the region very close to the threshold was not measured in detail. However, single tests made near the threshold showed that for these surfaces these sensitivity curves are tangent to the zero axis.

Of interest is the fact that reducing the thickness of the oxygen film shifted the threshold still farther to the red, that is to 7500A (4.0×10^{14} sec^{-1}), and then the further removal of the film shifted the threshold back to 5880A (5.1×10^{14} sec^{-1}) or nearly back to the value found in the first cell.

The maximum photoelectric emission per unit light intensity of the surface with a thick oxygen layer and that of the same surface after being heated to 1100° C was about one-seventh that of the surface after most of the oxygen had been removed by heating to 1600° C. This latter surface had a photoelectric emissivity about equal to that of the pure potassium film on tungsten.

Throughout the investigation it was noted that after heating the filament, and thereby removing the potassium and some of the oxygen, from 24 to 48 hours elapsed before the characteristics of the surface became constant.

Discussion of Results

Evaluation of surface fields from experimental data.

As previously stated, a considerable portion of the work function of metal surfaces can be accounted for by assuming that the field through which an electron leaves the surface is that due to its own image in the metal. This was considered by Lennard[6] and Debye[7] and discussed in detail by Schottky.[8] If an electron is at a distance x from the surface, its image produces a field E_i of magnitude,

[6] P. Lennard, Ann. d. Physik **8**, 149 (1902).
[7] P. Debye, Ann. d. Physik **33**, 441 (1910).
[8] W. Schottky, Phys. Zeits. **15**, 872 (1914).

$$E_i = -\frac{e}{(2x)^2} = -\frac{e}{4x^2}. \tag{1}$$

The potential of the image field at the distance x from the surface, considering the zero potential to be at $x=\infty$ with no accelerating field, would be:

$$V_i = -\int_{\infty}^{x} E_i dx = -\int_{\infty}^{x} \frac{-edx}{4x^2} = -\frac{e}{4x}. \tag{2}$$

Now if an external accelerating field E_a be applied, its potential at a distance x from the surface would be:

$$V_a = -E_a x \tag{3}$$

and the potential resulting from the two fields, the sum:

$$V = -\frac{e}{4x} - E_a x. \tag{4}$$

To find the maximum potential, the derivative of Eq. (4) may be equated to zero which is the same as equating the resultant field to zero.

$$-\frac{dV}{dx} = E = -\frac{e}{4x^2} + E_a = 0. \tag{5}$$

Solving for the value of x at the maximum:

$$x_{\max} = \frac{1}{2}\left(\frac{e}{E_a}\right)^{1/2}. \tag{6}$$

Substituting this value in (4) gives the value of the maximum potential:

$$V_{\max} = -\frac{e}{4}2\left(\frac{E_a}{e}\right)^{1/2} - \frac{E_a}{2}\left(\frac{e}{E_a}\right)^{1/2} = -(eE_a)^{1/2}. \tag{7}$$

Since the potential of the free electron has been chosen as zero, $(eE_a)^{\frac{1}{2}}$ represents the reduction in the maximum of the potential energy curve due to the applied field E_a. If the image forces were the only ones acting on an electron leaving the surface, this reduction in potential would represent the reduction of the work function of the surface.

This simple explanation will not hold for all distances from the surface, since the integral in Eq. (2) becomes infinite for $x=0$, which would represent an infinite work function. However of course for distances of atomic magnitude from the metal, the image forces no longer are of this form. The precise manner in which the field departs from the ideal image law is of no consequence to the present discussion.

Regardless of the assumed law of force near the surface of the emitting metal, an increase in the strength of the accelerating field will reduce the work function of the surface. When an electron is leaving the surface of a metal under the combined action of the surface fields and an accelerating field, it is

retarded until it reaches a distance from the surface x_1 where the applied field equals the surface field. As soon as it passes that point it is free and is accelerated from the surface. If the accelerating field is increased by an amount ΔE_a in es units, the field which the electrons must overcome is reduced by an equal amount, and since the electrons must work against this field for a distance x_1 to escape, the decrease in energy necessary for unit charge to escape would be:

$$-\Delta\chi = x_1 \Delta E_a. \tag{8}$$

Where $\Delta\chi$ is the change in the work function due to the change in the applied field ΔE_a. Dividing Eq. (8) by ΔE_a and considering the limit as ΔE_a approaches zero:

$$\frac{d\chi}{dE_a} = -x_1. \tag{9}$$

Thus observations on changes of the work function in strong fields yield directly the magnitudes of the electric fields near the surfaces. This method of evaluation of surface fields is due to Becker and Mueller.[9]

The above holds for any kind of electron emission, and the photoelectric threshold frequency gives a convenient measure of the work function as given by the Einstein relation:

$$h\nu_0 = e\chi. \tag{10}$$

Differentiating Eq. (10) and solving for $d\chi$ one obtains

$$d\chi = \frac{h d\nu_0}{e}. \tag{11}$$

Substituting the value of $d\chi$ from (11) into (9)

$$\frac{d\nu_0}{dE_a} = \frac{x_1 e}{h}. \tag{12}$$

Or expressing the field E_v in volts per centimeter:

$$\frac{d\nu_0}{dE_v} = -\frac{x_1 e}{300h} \text{ or } x_1 = -\frac{300h}{e}\frac{d\nu_0}{dE_v}. \tag{13}$$

Thus the distance from the surface x_1 where the applied field equals the surface field, is proportional to the slope of the ν_0 *vs.* E_v curve, evaluated at the particular value of the field in question.

This method of determination of the surface fields is independent of an exact measurement of the threshold, and depends only on the measurement of the displacements of the threshold. These displacements were measured a short distance away from the zero current axis, where the slopes of the curves were greater and the accuracy of the current measurements better.

[9] See ref. 2.

This procedure was justified because the electric fields produced a parallel displacement of the curves. The shifts could thus be determined with considerable accuracy.

In Fig. 5 curve A shows the Schottky shift as calculated from Eq. (7) making allowance for the change in units. Curve C shows the shift of the threshold of the pure potassium surface from the data of Fig. 2. The sur-

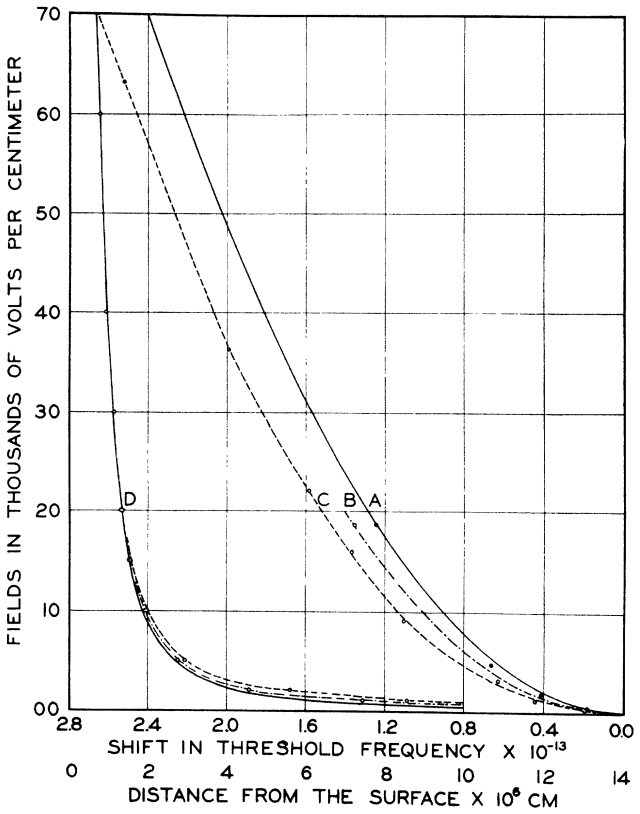

Fig. 5. Curves A to C show the shift of the threshold as a function of the field. Curve A the Schottky shift; C, the shift for the pure potassium surface; B, the shift for the surface heated to 1600° C, and the black dots the shifts for the surface heated to 1100° C. The curves D show the fields near the surface as a function of the distance from the surface. The type of line indicates the curve A to C from which it was deduced.

face with a thick oxygen layer showed negligible shift and was not plotted. The shifts measured from the curves A to D Fig. 4 were so nearly the Schottky values that the displacements are shown by the black dots only. This was the surface produced by heat treatment at 1100° C. Curve B shows the displacements measured from curves E to G Fig. 4, and shows the displacements of the threshold of the surface after being heated to 1600° C. From the three curves only two displacements could be measured, but

since both of these fell about midway between the theoretical curve and curve C, it was assumed that the complete curve was about as drawn.

The curves marked D show the fields calculated from the slope of the experimental curves B and C as compared with a calculated image field, drawn as a solid line. The single circles above fields of 20,000 volts/cm show the fields calculated from curve C. They show that the fields are very closely image fields between 7×10^{-7} and 1.2×10^{-8} cm from the surface. At greater distances, the fields of the two surfaces are greater than image fields. The field near the surface after it was heated to 1100° C is about the image field, and apparently the surface with a thick layer of oxygen under the potassium had only negligible fields which could be overcome by the applied fields.

It is of interest to note how closely the observed surface fields coincide with the image field within 1.2×10^{-6} cm of the surface. The deviation at greater distances is undoubtedly real though small. It is very small compared to the large deviations noted by Becker and Mueller,[10] Reynolds[11] and others for thoriated tungsten surfaces.

The possible sources of fields greater than the Schottky fields at large distances from the surface have been discussed by many investigators.[12] The best explanation seems to be that the potassium film is not uniform over the surface, so that there are areas of different work functions. The areas of lower work function are electropositive with respect to those of higher work function. The electrostatic fields between these areas are in sach a direction as to retard electrons leaving the surface through areas of lower work function. Near the threshold frequency, only the areas of lower work function are able to emit, and these electrons emerge with a retarding field equal to that of their image plus that due to the potential differences on the surfaces. The image field falls off as the square of the distance from the surface, while the fields due to these patches fall off much more slowly. Over the center of such a patch the field would be essentially constant to a distance comparable with about one-tenth of the diameter of the patch. Thus the extra field might be negligible compared to the image field near the surface and at greater distances become larger than the image field. It should be emphasized that to account for the deviation from Schottky fields at distances of 5×10^{-6} cm from these surfaces, it is necessary to postulate the existence of patches having a diameter about ten times this magnitude. Irregularities of atomic dimensions such as unequal distributions of ions over the surface as has been proposed by Suhrmann[13] are not capable of accounting for the experimental facts.

Since the film of potassium on the layer of oxygen which removed the

[10] See ref. 2.

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

[12] O. W. Richardson and A. F. A. Young, Proc. Roy. Soc. **A107,** 377, (1925). See also work of Becker and Mueller, ref. 2, that of Reynolds, ref. 10, and of B. Gudden, Naturwissenschaften **16,** 547 (1928).

[13] R. Suhrmann, Naturwissenschaften **16,** 616 (1928).

threshold farthest to the red exhibited very closely the Schottky field, it follows on this view that such films are homogeneous, and free from patches. In other words, the ions are distributed uniformly over the surface. Moreover it follows that the alkali film surfaces of the present experiments were much more homogeneous than the surfaces of thoriated tungsten studied by Becker and Mueller, Reynolds and others.

It is not evident why the surface with a thick oxygen layer should fail to show a reduction in the work function when the accelerating field is applied. There are two possible explanations. One is that the ions are about 300 atom diameters out from the surface of the tungsten, and the field between the positive potassium layer and the tungsten counteracts the image field in this region. At distances farther out, the image field is small and the counteraction of this by the applied field would not shift the threshold appreciably. The other postulates that the thick oxide layer is extremely rough, and the applied field can lower the work function of only the highest points, and since these constitute only a small part of the area, their emission would not appreciably affect the observed threshold. The principal part of the emission would occur from the hollows where the externally applied fields would be always greatly reduced. The small increase in the field would greatly assist the electrons emitted in the cavities to emerge without striking the walls of the cavity. This latter explanation seems to be more probable since this surface showed much poorer saturation than any of the others.

Comparison with theories of the photoelectric effect.

For the several surfaces and the many surfaces fields, i.e. the many thresholds studied in the present experiments the shape of the photoelectric sensitivity curves remained the same. Thus the form of the curve is practically independent of such superficial factors as the form of potential barriers at metal surfaces and therefore is of interest theoretically as well as experimentally.

From the standpoint of the wave mechanics, Wentzel[14] has calculated the rate at which free electrons in a metal are excited to higher energy states which enable them to escape over the potential wall of a metal surface, when light falls on that surface. He finds that this rate rate Z for light of frequency ν having electric vectors proportional to E_x, E_y, E_z incident on a metal surface with the normal along the x direction is:

$$Z \sim \frac{1}{\nu^{7/2}}\xi^2\left\{E_x^2 + \frac{m}{2h\nu}\left[\frac{1}{2}\xi^2E_x^2 + \eta^2E_y^2 + \zeta^2E_z^2\right] \cdots\right\} \qquad (14)$$

where ξ, η, ζ are the velocity components of the electrons before the excitation by the light. He derived an expression for the total photoelectric emission from a surface by integrating the above expression over the distribution of energies of the electrons in the metal. In order to obtain approximate

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

expressions he assumed the distribution of energies to be the Fermi-Dirac distribution at the absolute zero of temperature—a distribution of the form:

$$n(\epsilon)d\epsilon = 4\pi\left(\frac{2m}{h^2}\right)^{3/2}\frac{(\epsilon)^{1/2}d\epsilon}{e^{(\epsilon-\bar{\epsilon})/kT}+1} \tag{15}$$

where $n(\epsilon)d\epsilon$ is the number of electrons having energies between ϵ and $\epsilon+d\epsilon$. It is seen that at absolute zero the number increases as the square root of ϵ to a sharp upper limit for $\epsilon=\bar{\epsilon}$, the maximum energy of the Fermi distribution above which no electrons exist. The expression for the probability of excitation of an electron in the metal by impinging light indicates that the probability varies approximately as the square of the velocity of the electron and as the frequency of the light to the inverse 7/2 power. The Fermi distribution clearly led then to a formula for the total emission as a function of the frequency, having a sharp rise from a threshold value corresponding to the minimum energy necessary for an electron, having the maximum energy $\bar{\epsilon}$ of the Fermi distribution, to escape from the surface. The formula obtained in the case $\nu_0<\nu<\nu_a$ is the following:

$$I \sim [\bar{\nu}^{5/2}-(\nu_a-\nu)^{5/2}]\nu^{-7/2}E_x^2 + \frac{1}{14}[\bar{\nu}^{7/2}-(\nu_a-\nu)^{7/2}]\nu^{-9/2}[3E_x^2+2E_z^2+2E_y^2]+\cdots \tag{16}$$

Where $h\bar{\nu}=\epsilon$, the maximum energy of the Fermi distribution at 0°K, $h\nu_a=\epsilon_a$, the energy required by an electron at rest in the metal to escape over the potential barrier, and $\nu_0=\nu_a-\bar{\nu}$ is the threshold frequency. For $\nu<\nu_0$ there is no emission, and for $\nu>\nu_a$, $I\sim\nu.^{-7/2}$ The maximum of the photoelectric sensitivity curve is in the interval $\nu_0<\nu<\nu_a$, and this comprises the frequencies used in the present research.

The above expression really gives the rate at which electrons in the metal acquire enough energy to emerge from the metal and of course is equal to the photoelectric emission provided that the excited electrons do not make an appreciable number of inelastic impacts before striking the surface of the metal normally. Houston[15] has pointed out this tacit assumption of electron elastic impacts in Wentzel's derivation and believes a more nearly correct estimate of the photoemission would take account only of the electrons having great enough energies in their velocity components normal to the surface to escape. Integrating then the expression over the distribution of velocities normal to the surface in excess of a minimum value requisite to overcome the potential barrier, Houston has obtained the following expression:

$$I\sim\left(\frac{\bar{\epsilon}}{h\nu}\right)^{1/2}\left\{\frac{E_x^2}{\nu}\left[1+\frac{\bar{\epsilon}}{2h\nu}\right]+\frac{E_y^2+E_z^2}{3\nu}\left[\frac{\nu-\nu_0}{\nu}\right]\right\}\left(\frac{\nu-\nu_0}{\nu}\right)^2 \tag{17}$$

where I is the photoelectric emission at 0°K, $\bar{\epsilon}$ corresponds to the maximum

[15] We wish to thank Professor W. V. Houston for allowing us to read an unpublished manuscript dealing with this point.

energy of the electrons in the degenerate Fermi distribution and ν_0 is the threshold frequency.

Wentzel[16] is in agreement with Houston on the necessity of taking account of the distribution in direction of the velocities of the electrons in the metal in computing the rate of emission and has modified his original expression (16) obtaining

$$I \sim 1/\nu^{7/2}\left\{\tfrac{1}{3}\bar{\nu}\left[\bar{\nu}^{3/2} - (\nu_a - \nu)^{3/2}\right] - \tfrac{1}{5}\left[\bar{\nu}^{5/2} - (\nu_a - \nu)^{5/2}\right]\right\}E_x^2 \qquad (18)$$

+ higher powers in $\bar{\nu}/\nu$ (for $T=0°\mathrm{K}$) which is essentially the same as Houston's formula in so far as the first term of the expansion in $\bar{\nu}/\nu$ is accurate.

It has been thought by some that photoelectric thresholds are sharp, and thus in accordance with Wentzel's formula[16] and that lack of sharpness is ascribable to experimental errors, such as those introduced by scattered light. Others have observed photoelectric sensitivity curves approaching the frequency axis with zero slope, as is the case in the present experiments.[17] A simple calculation shows that the rounding off introduced by the temperature effects accounts for about half of the observed lack of sharpness of the thresholds in the present experiments, if Wentzel's first method of calculation be assumed. *Houston's calculation* (Eq. (17)) *corrected for temperature effects is adequate to account for nearly the whole tailing off of the here recorded sensitivity curves.* In a later experiment it is hoped to verify the calculated magnitude of the temperature effect by studying the sensitivity as a function of the temperature.

Fowler[18] has discussed the sharpness of photoelectric thresholds in a manner similar to Wentzel's original deduction, and therefore Houston's objections apply equally well to Fowler's conclusions that thresholds are sometimes sharp.

It has been mentioned that electrons can pass through regions of potential greater than that corresponding to their energy. The magnitude of the effect of applied fields at a metal surface is contained in the following formula:[19]

$$D(W) = \frac{4\left[W(W-\epsilon_a)\right]^{1/2}}{\epsilon_a} e^{-4\kappa(\epsilon_a - W)^{3/2}/3Ee}, \qquad \kappa^2 = \frac{8\pi^2 m}{h^2} \qquad (19)$$

where $D(W)$ is the probability that an electron with an energy W for the component of its velocity normal to the surface, will pass through a potential barrier whose maximum is ϵ_a volts greater than the zero of energy in the metal, when an accelerating field E is applied. For the maximum field, 63,000 volts/cm, used in the present experiments and assuming ϵ_a to be 7 volts, the probability $D(W)$ that an electron whose kinetic energy W is nor-

[16] We wish to thank Professor Wentzel for this information sent to us in a private communication.

[17] For discussion of this see B. Gudden, Lichtelektrische Erscheinungen, p. 37ff. Berlin, 1928.

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

[19] See ref. 1.

mal to the surface is 0.1 volt less than ϵ_a, the amount required to go over the potential barrier, is less than 10^{-15}. It is evident therefore that this type of influence of the shape of the photosensitivity curve was inappreciable for the fields used in the present experiments. A more favorable case for the observation of this influence of strong fields on photoelectric emission would be that of a metal having a high work function like pure tungsten where much higher electric fields may be applied before the autoelectronic current becomes appreciable.

The changes of the whole photoelectric sensitivity curves produced by applied accelerating fields observed in the present experiments are of fundamental interest, for the effect of the applied fields is to alter the work function without affecting any other characteristics of a metal concerned in its photoelectric properties. Both Wentzel's and Houston's formulas agree in indicating that over the present range of observation the whole photoelectric sensitivity curve shifts by approximate parallel displacement along the frequency axis with the threshold. Alteration of the nature of the work function (the surface electrostatic fields) does not affect markedly the form of the sensitivity curve. *This prediction of the wave mechanical theory of the photoelectric effect is strikingly confirmed in the present experiments.*