SEPTEMBER 1, 1932 PHYSICAL REVIEW VOLUME 41

The Photoelectric Properties of Alkali Metal Films as a Function of their Thickness

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(Received May 11, 1932)

Previous workers have given very little consideration to the thickness of the alkali metal films under investigation. The purpose of the present work was to study the photoelectric properties of the films as a function of their thickness. A molecular beam was used to deposit a computed number of alkali metal atoms on a silver surface cooled with liquid air. In this way, films of various thicknesses were formed and their corresponding spectral response curves taken. The recorded thresholds were arbitrarily chosen as the points, where the currents became definitely measureable. For potassium, the maximum threshold, approximately 5800A, occurred at a film thickness of 3.0 molecular layers while the maximum total photoelectric emission occurred at 12.4 molecular layers, and the photoelectric properties remained constant after 19.0 molecular layers. The atomic spacing in the monomolecular layer is assumed to be the same as that in a solid mass of alkali metal. The threshold for the thick film was approximately 5500A. For rubidium, the maximum threshold, approximately 6200A, occurred at a film thickness of 1.5 molecular layers, while the maximum total photoelectric emission occurred at 5.0 molecular layers, and the photoelectric properties remained constant for film thicknesses beyond 12 molecular layers. The threshold for the thick film was approximately 5900A. For caesium, the maximum threshold, approximately 6600A, occurred at a film thickness of 1.5 molecular layers, while the maximum total photoelectric emission occurred at 5.0 molecular layers, and the photoelectric properties remained constant for film thicknesses beyond 10.0 molecular layers. The threshold for the thick film was approximately 6300A. Some anomalous effects are reported in the case of sodium. The maximum extension of the threshold was found to be much less than that reported by other investigators. A theory is advanced to account for the existence of a maximum in the excursion of the threshold.

PREVIOUS workers[1,2,3] have shown that large changes of the photoelectric properties of metal surfaces are produced by the deposition of thin alkali metal films but little has been done to study these effects quantitatively.

The present work was therefore undertaken for the purpose of studying the photoelectric effect as a function of a known number of deposited alkali metal atoms. One of the essential features of this work was the use of a molecular beam for controlling the amount of alkali metal deposited to form the film. The atoms were ejected from a pinhole opening in a reservoir containing the alkali metal, and allowed to condense on a metallic surface cooled with liquid air. The process was carried out in a very high vacuum. By using

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

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

[3] Ives and Olpin, Phys. Rev. **34**, 117 (1929).

this method, the chances for a uniform deposit were increased, and the calculation of the number of deposited atoms was possible.

Another feature of this work was the attempt to obtain a gas-free metallic surface on which to form the alkali metal film. This was done by evaporating the underlying metal under high vacuum conditions just before the alkali metal atoms were condensed on it.

The method proved successful in obtaining films of any desired thickness, which, although allowed to stand for several hours, showed no variation in photoeffect.

APPARATUS AND EXPERIMENTAL PROCEDURE

A number of cells were constructed, with gradual modification of details, until the final form shown in Fig. 1 was adopted.

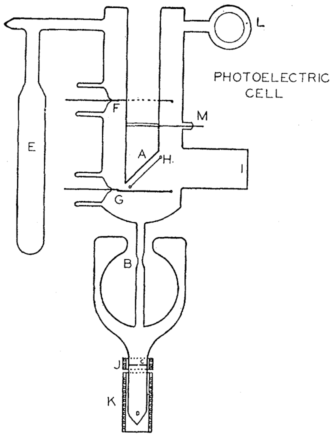

Fig. 1. Diagram of photoelectric cell.

The lower portion of the tube, *D*, acted as a reservoir for the alkali metal. It was separated from the rest of the tube by a thin glass partition with a pinhole (made by piercing the glass with a heated 30-mil tungsten wire which had been pointed on the end) in the center, *C*. That portion of the tube, *B*, just above this, was devoted principally to a container for liquid air which was used in defining the beam of alkali metal atoms. The constriction in the central tubing acted effectively as a defining slit for the beam, while the liquid air eliminated the possibility of reflection from the walls of the tubing. The condensation surface, *A*, was made from a glass tubing which was sealed off at one end and pressed against a slab of carbon while hot, so that the surface made an angle of 45° with the long axis of the tube. This formed a container into which liquid air could be placed. The purpose of this device was to insure the condensation of every alkali metal atom, and at the same time, to lower the pressure in the tube.

F and *G* were 15-mil tungsten filaments wrapped with No. 30 B and S gauge silver wire. By passing a current through these filaments, silver was evaporated over the inside surface of the tube. This acted as a shield from electrostatic charges and as the underlying conducting surface for the deposit of the alkali metal atoms.

A grid, *H*, consisting of five 6-mil tungsten wires, spot-welded to 50-mil tungsten leads, served to pick up the photoelectrons. A guard ring was mounted inside of the tube through which the grid wire leads were brought out.

The tube, which was made of Pyrex glass, was exhausted to a high vacuum by means of a mercury diffusion pump working through a liquid air trap. A separate heater was used to bake out the charcoal in the side tube, *E*, which was raised to the softening point of glass while the rest of the tube was baked out at 450°C.

Due to the large amount of vapor and gas emitted from the heated charcoal, it was given a preliminary bake-out before the tube containing the alkali metal was connected. After the preliminary bake-out, air was allowed to pass into the cell through the liquid air trap, and the tube, containing the salt and calcium, was sealed on as quickly as possible. The cell was then reevacuated and baked out simultaneously with the charcoal trap for a period of 15 or 16 hours. The plate and grid of the ionization gauge were brought to a red heat by means of electrical bombardment, and remained in this state until no more gas was given off. This usually lasted for about an hour.

The inside of the tube was then given a coating of silver by passing a current through the filaments wound with silver wire. This process was performed very slowly (several hours), in order to outgas the silver. Contact was made to the silver coating by means of "cat whiskers" of tungsten wire, spot-welded to the tungsten leads. Four of these contacts were used to insure electrical connection. Silver wire, wrapped around the tube on which the alkali metal was deposited, and brought out to the tungsten lead, *M*, was also used for this purpose.

The alkali metal, which was vacuum distilled through several constrictions during the bake-out, was finally driven into the lower portion of the tube. The photocell was then sealed off from the vacuum system and tested.

In studying the photoelectric effect, a 6-volt, 110-watt, tungsten ribbon filament lamp was used as a source of light. By means of a lens this light was focused on the slit of a Van Cittert-type double monochromator. An achromatic lens was used to focus the dispersed light on the photocell. The photoelectric current was measured with a Compton quadrant electrometer having a sensitivity of 4000 mm per volt at one meter scale distance.

The temperature of the alkali metal was controlled by means of the heating coil, *K*. The pinhole was heated by another coil, *J*, and the temperature at this point was kept several degrees higher than the lower part of the tube, to prevent condensation at the small opening. Chromel-Alumel thermocouples were used to determine the temperatures. The hot junctions were held in contact with the glass by wrapping copper foil about them. The thermocouples were calibrated from the freezing point of water and the boiling point of water, naphthalene, diphenylamine, and sulfur. The temperatures could be determined to 1°C.

After placing the tube in position in front of the monochromator, the containers *A* and *B* of the photocell, and the Dewar flask which was placed on the charcoal trap, were filled with liquid air. The ionization gauge was then connected so that the pressure in the cell could be determined. The plate current was measured by means of a galvanometer having a sensitivity of 3×10^{-9} amperes per mm deflection at a scale distance of one meter. With a grid current of 5 milliamperes, pressures producing currents as low as 1.5×10^{-9} ampere were obtained. The gauge indicated no change in the vacuum when heat was applied to the alkali metal reservoir.

After liquid air was placed in the containers *A*, *B*, and the Dewar flask, the cell was allowed to stand for several hours in order to give the vacuum time to improve. When the pressure in the tube had reached a value in the order of 10^{-8} mm of Hg, a current was passed through the heating coil, *K*, and the temperature brought up to a constant value. The usual procedure was to allow the temperature of the heater to reach its final value before placing it over the alkali metal reservoir. This plan was adopted in order to reduce the time taken for the equilibrium temperature to be reached. The heater was then left over the alkali reservoir for a definite period, and then removed. The temperature of the reservoir dropped immediately after the heater had been removed.

When there was a sufficient deposit to give a detectable photoeffect, the film was studied by means of a spot of nearly monochromatic light (about 20A), which was focused on the plate. The deposit of alkali metal was explored by examining the photocurrent as the light passed over different parts of the film. In this way, it was found that the deposit was quite uniform and sharply defined at the edges. The position of the light beam was varied by moving the achromatic lens, which was placed between the photocell and the monochromator. The film was then allowed to stand for several hours to test for any change in the photoelectric sensitivity. In the meantime, the proper containers were kept filled with liquid air. When the vacuum was in the neighborhood of 10^{-8} mm of Hg, and the alkali deposit had been made on a freshly evaporated surface of silver, there was found to be no variation in the photoeffect even after the tube had been left standing for several hours. A spectral distribution curve was taken for this particular surface, and the heater again applied to the lower part of the tube for a definite time. In this way any desired thickness of film could be investigated.

In order to begin a new set of measurements, the lower silver filament was heated and the silver evaporated over the surface until no photoeffect could be detected, even in the presence of a very strong light.

The distribution in energy throughout the spectral range was determined by placing a vacuum thermopile in front of the monochromator in the position usually occupied by the photocell. The thermopile galvanometer deflections were amplified by means of a photoelectric cell relay arrangement in order to determine the distribution in the blue part of the spectrum, where the energy was low. The data obtained in this way were used in plotting the spectral response curves on an equal energy scale.

Calculation of Film Thickness

The formula used to determine the number of deposited alkali atoms was taken from an article by O. Stern.[4]

$$q = (5.83 \times 10^{-2})pf/(MT)^{1/2}$$

where q represents the number of moles ejected in one second from the pinhole, C; M is the molecular weight of alkali metal; T the temperature, Kelvin, of the alkali metal reservoir; p the vapor pressure, in mm of Hg, of alkali, at temperature T; f the area of the pinhole in cm^2.

If J represents the number of moles striking the condensing surface in one second, then

$$J = q/\pi r^2,$$

where r is the distance in cm from the pinhole to the surface on which the deposit is formed.

The number of atoms striking the surface in one second, is given by the equation,

$$N = (6.06 \times 10^{23})qJ.$$

It is inconvenient, in referring to the film thickness, to state the number of atoms deposited. Instead, a definition for a molecular layer will be given, and this expression used in reference to the thickness.

In a solid mass of metal, the number of atoms per cm^3 can be determined by dividing the density of the metal by the mass of a single atom. The cube root of this number gives the number of atoms along an edge, and the square of this quantity gives the number of atoms per cm^2. This will be used as a definition for a molecular layer. It is understood, however, that in forming a very thin film, the spacing may be quite different from that in a solid mass of the metal. A discussion of the number of atoms per cm^2 in monatomic layers has been given by Becker.[5]

The diameter of the pinhole was 0.75 mm and the distance from the pinhole to the condensation surface was 16.0 cm.

The vapor pressure of potassium was obtained by use of the empirical formula of Edmondson and Egerton[6] and for sodium, the formula given by Rodebush and de Vries[7] was used. The probable error as estimated by these experimenters is less than 5 percent.

The vapor pressures of rubidium and caesium were determined from the values of the constants given in the International Critical Tables.[8] The vapor pressures can be determined within 10 percent by means of these values.

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[4] O. Stern, Zeits. f. Physik **39**, 754 (1926).

[5] J. A. Becker, Phys. Rev. **28**, 341 (1926).

[6] Edmondson and Egerton, Proc. Roy. Soc. **A113**, 526 (1928).

[7] Rodebush and de Vries, J. Amer. Chem. Soc. **45**, 2323 (1923).

[8] International Critical Tables III, 205.

However, this accuracy is uncertain inasmuch as there is a wide variation in values given by different experiments.[9,10] This has been pointed out by Rowe.[11]

The principal variable errors in the experiment were the measurement of the temperature of the alkali metal reservoir and the length of time it was heated. The error in the determination of the film thickness caused by the variation in temperature (after the reservoir had reached equilibrium temperature) was probably not more than 4 percent. The determination of the time of heating was made a little uncertain by the fact that it required a few minutes to reach the equilibrium temperature after the heater was applied to the reservoir. This error was not usually more than 10 percent. The total variable error then was probably less than 12 percent.

Constant errors may have been introduced in the calibration of the thermocouple and the measurement of the hole and distance between the hole and condensation surface. It is likely that the total constant error was less than 6 percent. The total error in the determination of the film thickness is probably less than 20 percent (this includes the possible error of 10 percent in vapor pressure).

EXPERIMENTAL RESULTS

Potassium

Curves showing the photoelectric current as a function of the wave-length of the incident light are illustrated for the different film thicknesses in Fig. 2.

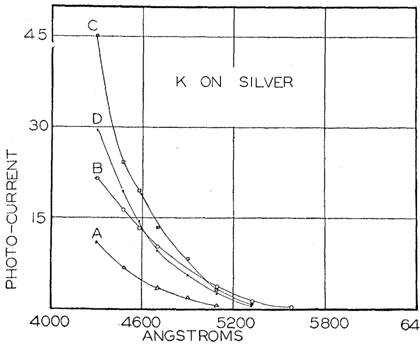

Fig. 2. Spectral response curves for different film thickness of potassium. *A*, 0.8 molecular layer; *B*, 3.0 molecular layers; *C*, 12.4 molecular layers; *D*, 19.2 molecular layers.

The ordinates represent photocurrent per unit light intensity in arbitrary units. The recorded thresholds were arbitrarily chosen as the points where the currents became definitely measurable.

A represents the spectral response curve for a film formed on a freshly coated silver surface, when the potassium reservoir was heated to a tempera-

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[9] D. H. Scott, Phil. Mag. **47**, 32 (1924).
[10] T. J. Killian, Phys. Rev. **27**, 578 (1926).
[11] H. Rowe, Phil. Mag. **3**, 534 (1927).

ture of 150° for 15 minutes. The computed thickness in this case was 0.8 molecular layer. The long wave-length limit was in the neighborhood of 5100A and the shape of the spectral response curve was different from that for heavier deposits.

The next curve, *B*, was obtained after reheating the potassium reservoir to 150°C for 35 minutes, which brought the computed thickness up to 3.0 molecular layers. The threshold shifted to the neighborhood of 5800A and the shape of the spectral response curve changed.

The heating coil was then replaced over the reservoir and the temperature brought up to 170°C (vapor pressure $=1.48\times 10^{-3}$ mm). After it was allowed to remain at this temperature for 60 minutes, the data for curve *C* were taken. This film gave the maximum total emission, although the threshold did not extend as far toward the red as that of curve *B*. The computed thickness was 12.4 molecular layers.

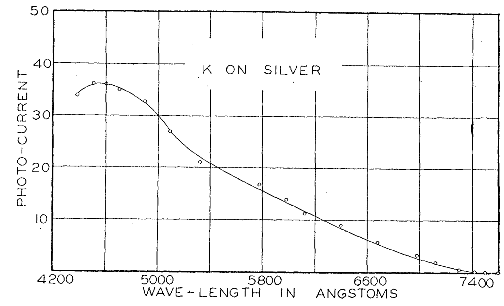

Fig. 3. Spectral response curve for contaminated potassium film.

Curve *D* was obtained from a film which was formed by reheating the potassium reservoir to 170° for 44 minutes. This film represented the thickness beyond which there was no further change in the photoelectric effect. The computed thickness was 19.2 molecular layers.

The curves were chosen from a set taken at various film thicknesses to illustrate the principal photoelectric changes which took place during the development of the film.

Separate experiments, in which different reservoir temperatures were used to secure the same film thickness, gave results which showed that the photoelectric effect was independent of the rate of deposition when varied as much as tenfold.

An attempt was made to study the films when the condensing surface was not cooled with liquid air, but the photoelectric effect did not remain constant after a deposit was made. There was a constant decrease in emission which indicated that changes were taking place on the surface.

The pressure in the photoelectric cell (measured with the ionization gauge) had to be in the neighborhood of 10^{-8} mm or less before consistent results could be obtained. In cases where the pressure was not this low, undesirable effects were noticed. One of these was the gradual decrease in emission just after the film was exposed to light. The original sensitivity could be restored by allowing the cell to remain in the dark for several minutes. This fatiguing was found to be greater in the case of illumination by violet than for longer wave-lengths. Successive exposures to light and darkness produced no change in the effect.

In order to make a test of the effect of increasing the pressure in a tube from which reliable data had been obtained, the liquid air was removed from the charcoal after a thin film was deposited. Fig. 3 illustrates the results found in a typical case. The curve was taken four hours after the liquid air was removed. The shape of the spectral response curve as well as the position of the threshold was greatly changed by the increase in pressure in the cell. The results were not quantitatively reproducible in a case of this kind, but indicated that the change in the photoelectric effect was greater for films in the order of a monomolecular layer than for heavier deposits.

Sodium

Several tubes were constructed in which silver was used as the underlying surface for the study of sodium films. It was found, however, that in each case, the photoelectric emission began to decrease immediately after the heating coil was removed from the sodium reservoir. The pressure in the tube was measured each time and found to be in the neighborhood of 10^{-8} mm. The instability of photoelectric emission could not, then, be attributed to a poor vacuum.

A cell was next constructed with nickel as the underlying material, but here again there was a decrease in emission after the film was deposited.

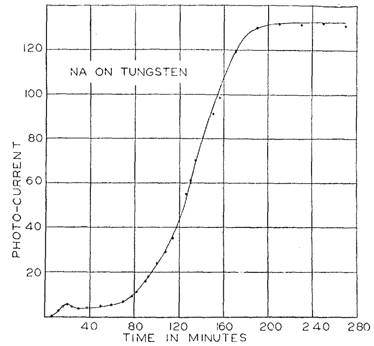

Fig. 4. *White light* curve for sodium. Rate of film formation, 1.1 molecular layers per minute.

Finally, a tube in which tungsten was used as the underlying material was constructed, and in this cell stable sodium films were formed. The emission from the thin films was found to be too small to be measured when the light from the monochromator was used, so a tungsten filament lamp, glowing at much less than its normal brilliancy, was used as a source. The *white light* curve, showing the emission as a function of film thickness, is illustrated in Fig. 4. In order to secure the data for this curve the sodium reservoir was heated to 270°C (vapor pressure $= 7.64 \times 10^{-3}$ mm) and the emission was recorded at intervals during the progress of the film development. The computed rate of film formation in this case was 1.09 molecular layers per minute.

A maximum appeared in the emission curve for a film thickness of 15 molecular layers. The emission was found to increase again for a computed film thickness of about 100 molecular layers. The magnitude of the emission in this case rose to a value about 25 times greater than the maximum for the very thin film. The film development, however, was not carried out far enough to determine definitely whether the emission remained constant or whether the large increase represented a second maximum.

This enormous increase in emission for deposits in the order of 100 molecular layers was not found in the other alkali films.

Rubidium

Fig. 5 shows the dependence of the photoelectric effect on the wavelength of the incident light for different film thicknesses. Curve *A* represents the spectral emission for a film formed by heating the rubidium reservoir to 110°C (vapor pressure $=4.06\times10^{-4}$mm) for 11 minutes. The computed thickness was 0.4 molecular layer. The threshold was in the neighborhood of 5800A.

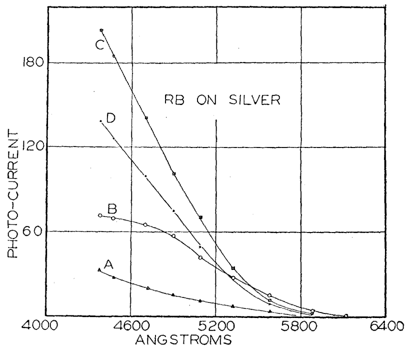

Fig. 5. Spectral response curves for different film thicknesses of rubidium. *A*, 0.6 molecular layer; *B*, 1.5 molecular layers; *C*, 5.0 molecular layers; *D*, 12 molecular layers.

The rubidium reservoir was then reheated to 110°C for 30 minutes. This brought the computed thickness to 1.5 molecular layers. The threshold lies in the neighborhood of 6200A and was farther in the red than for any other thickness. The shape of the curve was quite different from that of the others and appeared to be nearing a maximum at 4000A.

The heating coil was again placed over the rubidium reservoir and the temperature raised to 130°C for 28 minutes. This brought the computed thickness to 5 molecular layers. This film gave the maximum photoelectric emission, but the threshold was not as far in the red as that for the preceding thickness.

The final curve, *D*, was obtained after reheating the reservoir to 130°C, and the atoms were allowed to condense for 58 minutes. This brought the computed thickness to 12 molecular layers. The emission was less than that for the preceding film, and the threshold shifted farther toward the blue. Further increase in deposition produced no change in the photoeffect.

Caesium

The results for caesium are illustrated in Fig. 6. For this element the region near the threshold was investigated more carefully than for any of the other metals. This region of the curves was magnified as shown in the right hand corner of the figure. The data beyond 5800A were secured by opening the slits of the monochromator so that the light intensity was increased. In doing this, the wave-length band was broadened from 20 to 40A. The curves are seen to approach the wave-length axis asymtotically, and the existence of an optimum thickness for the maximum extension of the threshold is definitely established.

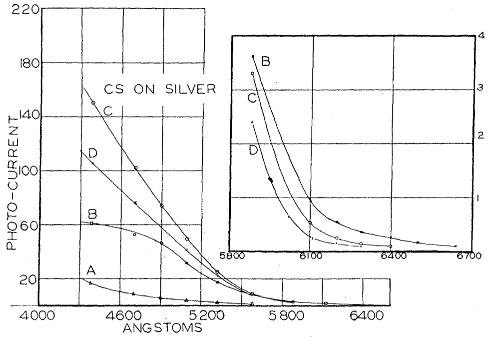

Fig. 6. Spectral response curves for different film thicknesses of caesium. *A*, 0.6 molecular layer; *B*, 1.5 molecular layers; *C*, 5.4 molecular layers; *D*, 10 molecular layers.

The results were very much the same as those for rubidium. Curve *A* was obtained after heating the caesium reservoir to 105°C (vapor pressure = 6.4×10^{-4} mm) for 12 minutes. This gave a computed thickness of 0.6 molecular layer. *B* represents data obtained after reheating the reservoir to 105° for 16 minutes. This brought the computed thickness to 1.5 molecular layers. This also represented the thickness for the maximum extension of the long wave-length limit.

As the deposition was increased, the emission increased, but the threshold receded toward the blue end of the spectrum. Curve *C* represents the thickness for maximum emission. In this case, the caesium reservoir was heated to 120°C (vapor pressure = 1.57×10^{-3} mm) for 33 minutes. This brought the computed thickness to 5.4 molecular layers.

Finally, the caesium reservoir was heated to 120°C for 43 minutes. This brought the thickness to 10.4 molecular layers. Curve *D* represents the spectral emission for this film.

DISCUSSION OF RESULTS

According to Sommerfeld's theory,[12] a metal may be considered as a box of free electrons which are kept within the enclosure by a potential wall at the boundary. These electrons obey the Fermi-Dirac statistics so that at the absolute zero of temperature there is a definite upper limit for the energy that an electron may have. The work function of the metal is then defined as the energy necessary to remove an electron from this highest energy state (at 0°K) entirely away from the metal. It appears as $h\nu_0$ in Einstein's photoelectric equation,

$$h\nu = mv^2/2 + h\nu_0$$

where h is Planck's constant, ν the frequency of the incident light, and v the velocity of the ejected electron and ν_0 the threshold frequency. Thus, the determination of the threshold is a measurement of the work function of the surface.

The *grid* theory of activated surfaces may be used to advantage to account for the effect produced by the thin alkali films. This theory has been investigated by Becker[13] in his work on thermionic emission. It has also been discussed by Compton and Langmuir,[14] who refer to it as the *adion field theory.*

The fact that alkali ions are evaporated from heated filaments which have been previously coated with a deposit of alkali metal, indicates that the deposited atoms behave like ions on the surface. Then in the present experiment, as the atoms condense on the silver surface they produce an ionic layer which sets up an electric field which aids the electrons in their escape from the metal. For a first approximation, the field due to this ionic grid may be considered uniform and proportional to the number of ions in the layer.

The upper diagram in Fig. 7 represents the potential curve for silver. The horizontal dotted line represents the highest Fermi energy state. The vertical line AA' represents the boundary of the silver so that the portion of the curve to the left of this line is the potential of the interior of the silver. The light solid line (a trough) to the right of A illustrates the effect of a very small deposit of alkali atoms (perhaps 1/50 of a molecular layer). As more atoms are deposited on the silver the bottom of this trough becomes lower but no electrons will remain in the trough until it is lower than the highest Fermi energy state. A calculation[15] of the electric field near the surface due to the ions (for potassium on silver) shows that it requires only 0.2 of a monomolecular layer of ions to reduce the work function from that of the pure silver surface to that of a very thick film of alkali metal. This indicates that the atoms all become ions as soon as they are deposited, up to 0.2 molecular, after which they go on as atoms. On the potential curve this means that it

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[12] A. Sommerfeld, Zeits. f. Physik **47**, 1 (1928).

[13] J. A. Becker, Bell Tech. Lab. Reprint B-412 (August 1929); Phys. Rev. **35**, 1431 (1930).

[14] Compton and Langmuir, Rev. Mod. Phys. **2**, 157 (1930).

[15] For method, see Hughes and DuBridge, *Photoelectric Phenomena*, page 86. (McGraw-Hill Book Co., 1932).

requires 0.2 molecular layer of ions to lower the trough to the highest Fermi energy level. For deposits less than this the electrons leave the trough and *spill over* into the silver. This theory is supported experimentally by the fact that the *threshold is shifted to within 85 percent of its thick-film value by a deposit of 0.2 of that required for the maximum excursion.**

This theory accounts very well for the extension of the threshold toward the red during the early stages of the deposit but does not account for the excursion of the threshold *beyond its value for the solid alkali*, nor for a *maximum in this excursion* for a thickness of a few molecular layers. However, Professor J. R. Oppenheimer has suggested the following possible explanation to the writer.

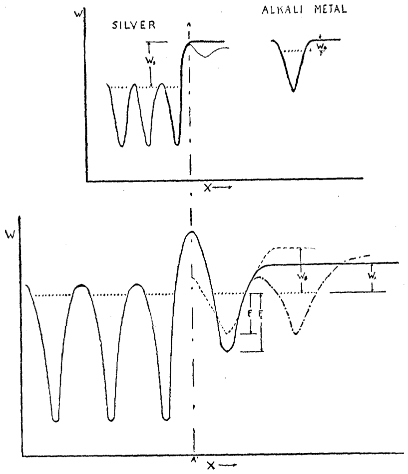

Fig. 7. Potential energy of an electron passing through silver and an alkali metal film; upper curve, before contact of metals. Lower, in contact.

The potential curve for an isolated monomolecular layer of alkali metal atoms is illustrated in the upper diagram of Fig. 7. This same curve is illustrated schematically as a dashed line in the lower diagram. It neglects the effect of the potential due to the silver. From this diagram it is seen that in this case (for potentials as drawn) the alkali metal potential trough *is narrowed* by the potential of the silver. If the wave mechanics is now applied to this *narrowed* trough to solve for the possible energy states in which electrons may exist, it is found that the states are distributed farther apart than in a normal trough. The distribution of energy states in a box of electrons depends upon the size of the box when its dimensions are in the order of a few atom diameters. F_2, in the figure, represents the total spread of energy values from the zero to the highest Fermi state. The work function, then, is W_A. The dashed line represents a normal potential trough (without the

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* The threshold for outgased silver is about 2600A while the thick film threshold for potassium on silver is about 5500A. This is a threshold shift of 2900A. A 0.6 molecular layer gave a shift of 2500A which is 85 percent of the 2900A shift.

narrowing effect produced by the proximity of the silver) and the work function in this case would be W_B. The total spread in energy states would be F_1.

For these same potentials the dash-dot line represents the effect of adding a second layer of atoms.

The course of the potentials schematically drawn in Fig. 7 is a wholly reasonable one, and would account simply for the observed excursion of the threshold.

Lawrence and Linford[16] have shown that the work function of a surface may be changed by the application of strong electric fields. Their experiment also showed that for a composite surface of potassium on tungsten this change in work function has very little effect on the shape of the spectral response curve. In other words, the curves are shifted very nearly parallel to themselves along the frequency axis. It might be assumed, therefore, that the difference in shape of the curves for different thicknesses (in the present experiment) was due entirely to a difference in the source from which photoelectrons originate. For instance, one might assume that in the early stages of the film development the electrons came principally from the underlying material but as the deposit increased beyond that necessary to form a monomolecular layer, the photoelectrons originate principally in the alkali metal. As the electron density in the two metals differs considerably, one might assume that the spectral response curve for the very thin film would be quite different in shape from that obtained for a thicker one.

An attempt was made to test this assumption by means of Houston's modified form of Wentzel's theoretical expression for the complete spectral emission of photoelectrons. The equation is given in the paper by Lawrence and Linford.

For deposits of a monomolecular layer or less in thickness, the value of ϵ (the maximum energy of the Fermi distribution at 0°K) was calculated from the electron density in silver. For a thick film the value of ϵ was calculated by using the electron density in the alkali metal.

The experimental values for the threshold found for the monomolecular film and the thick film were used in Houston's expression, and two theoretical curves were plotted for photoelectric current against frequency of exiting light. The shapes of these curves were then compared with the two experimental curves (monomolecular layer and thick film). According to this theory the emission from silver should be greater than from the alkali, (using the reduced value for the work function), but experimentally the emission was found to increase for films greater than a monomolecular layer. This discrepancy between Houston's theory and the present results might possibly be ascribed to Houston's failure to correct adequately for the binding of the conduction electrons in silver.

Also, the experimental curves for rubidium and caesium for a thickness in the order of a monomolecular layer appear to approach a maximum near

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[16] Lawrence and Linford, Phys. Rev. **36**, 482 (1930).

4000A and the calculated maximum (Houston's formula) is nearer 3000A and is slightly farther in the violet for silver than it is for the alkali metal.

Hughes and DuBridge[17] have shown that the theory gives a curve which is of approximately the correct shape near the threshold, but at higher frequencies departs widely from the form of the curve obtained experimentally for the alkali metals.

No conclusion can be drawn on this point until a more exact theoretical expression is obtained for the total spectral emission.[18]

In general the results of the present investigation show the same phenomena as that reported by previous workers. However, there are two important differences. One is the difference in film thickness between that found for the maximum total emission and that for the maximum extension of the threshold. The other difference deals with the magnitude of the maximum excursion of the threshold. Ives and Olpin[19] found shifts in the order of 1000A in going from the thickness of maximum threshold to the thick film. In the present work the shifts were in the order of 300A. This difference may be due to the fact that the underlying material in the present experiment was freshly evaporated while Ives and Olpin used a solid plate of metal. It is thought that the use of a freshly evaporated underlying surface minimized the possibility of occluded gas on the surface. This is based on the fact that larger shifts in the threshold were found when the silver surface was allowed to stand a day before depositing the alkali metal. The recorded shifts were obtained by depositing the alkali metal immediately after evaporating the silver.

In conclusion the author wishes to thank Professor E. O. Lawrence for proposing the problem and for his suggestions and constant interest throughout the course of the work.

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[17] Hughes and DuBridge, *Photoelectric Phenomena*, page 228.

[18] Ives and Briggs in a recent paper (Phys. Rev. **40**, 802 (1932) have presented evidence that indicates that the photoelectrons originate partly in the underlying metal and partly in the alkali metal film, the relative proportions varying with the film thickness.

[19] Ives and Olpin, Phys. Rev. **34**, 117 (1930).