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EFFECT OF ELECTRIC FIELDS ON THE EMISSION OF PHOTOELECTRONS FROM OXIDE CATHODES

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ABSTRACT

A study has been made of the photoelectric emission obtained at room temperature from the equipotential oxide cathodes commonly employed in radio receiving tubes. With a double monochromator, long-wave limits were determined by plotting the currents as a function of the wave-length of the incident radiation. The threshold frequencies decreased with increase in the accelerating potential according to the relation,

$$\nu = \nu_0 - bE^{1/2},$$

in which ν_0 is the "zero-field" threshold and E the electric field at the cathode surface. It is shown that the observed lack of saturation in the photo-currents may be ascribed to a decrease of work function with increase of applied field. The tendency to non-saturation is greatest for light of longest wave-length. Calculations show that the photoelectric equation of Houston satisfactorily represents the variation in numbers of emitted electrons with color of illumination, and with change of threshold. Some comparisons are made of the photo-emission and the thermionic currents obtained from the same cathode surface. There is a change in photoelectric threshold with activation. Preliminary measurements of thermionic work functions confirm the theory that in both cases the emission of electrons takes place from the outermost layers of the oxide coating.

INTRODUCTION

THE oxide-coated type of thermionic emitter is the most economical source of electrons at present available for use in commercial radio receiving tubes. Although it has been developed to a point of high efficiency in the technical laboratory, relatively little is known concerning the atomic processes which take place during the formation of the coating, and no completely satisfactory analysis of the mechanism by which electrons are released from the oxide has been made. Many investigators have studied the thermionic properties of the coating, but not a great deal of information is available concerning the photoelectric characteristics of this type of emitting element. The present paper is concerned chiefly with considerations of the surface structure of such coatings as revealed by a study of their photoelectric properties.

Results of recent investigations have raised the question as to the localization of the active elements of the coating which give rise to its high electron emissivity. The commercial form of coating is prepared from a fifty-fifty mixture of barium and strontium carbonates, which, after deposition upon a metal filament, is reduced to the oxide form. It has been definitely established that when the coating becomes an active emitter, atoms (or ions) of barium and strontium are released from the oxide crystals and held in the form of "free" or adsorbed metal somewhere within the coating, or upon its outer surface. Presumably these atoms and ions constitute emission centers of low work function for electrons, but as to the exact nature of their action various investigators are not in agreement.

Lowry[1] has studied the effect of coating different metals with the same mixture and finds that the emission depends markedly upon the type of core metal used. He concludes that the thermionic efficiency is determined by the kind of surface formed at the interface between core metal and coating, and that the alkaline earth atoms which serve as active emission centers are those which are deposited upon the core metal surface. Reimann and Murgoči[2] also conclude from their experiments that the electrons are emitted from the barium metal adsorbed on the core. The results reported by Becker[3] and others,[4] on the contrary, lead to the conclusion that the alkaline earth metal is adsorbed in a layer on the superficial outer surface of the coating itself.

It was felt that an examination of the photoelectric emission from the oxide would yield results of particular value concerning the structure of its outer surface, and, by comparison with the thermionic properties of the coating, give definite information as to the activation and adsorption processes which occur.

It is a fact of common experience that well saturated electron currents cannot be obtained from an oxide coated cathode. As to the explanation of this effect, various investigators are not in agreement. Lowry[1] suggests that the process of electron diffusion through a porous coating may account for the phenomenon of non-saturation. Many writers believe that this effect in the case of composite surfaces, over and above that which may be accounted for on the basis of Schottky's electron image theory, is due to the neutralization of local surface fields by the fields applied to the cathode. Of the various hypotheses so far proposed as to the nature of these intrinsic fields, none is eminently successful in explaining the observed dependence of emission upon accelerating potential.

In order to establish a satisfactory theory, it is evident that more information on emission characteristics of composite surfaces is required. To this end, a number of data were obtained during the course of the present investigation on the photo-currents from oxide cathodes over a wide range of potentials and under various conditions of illumination. It was found that the tendency to non-saturation is particularly marked in the photo-emission as measured at room temperature, and that the effect is a function of the color of light used. It was also observed that the photoelectric threshold shifts in a

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[1] E. F. Lowry, Phys. Rev. **35**, 1367–78 (1930).

[2] A. L. Reimann and R. Murgoci, Phil. Mag. **8**, 440 (1930).

[3] J. A.Becker, Phys. Rev. **34**, 1323–1351 (1929).

[4] Cf. Saul Dushman, Reviews of Modern Physics **2**, 431–441 (1930).

definite manner with applied field. On the basis of these experimental facts it is obvious that any attempt to explain the continued rise in emission with increase of accelerating potential must take into account the frequency of the incident radiation as well as the value of the applied field. It is believed that a satisfactory correlation of the effect of applied fields on saturation current values and the observed shift in long-wave limit has been obtained. In any case, the data obtained should furnish a basis for further investigations of the photoelectric properties of oxide cathodes.

EXPERIMENTAL DETAILS

The coatings studied were precipitated mixtures of barium-strontium carbonates commonly used in the manufacture of commercial radio tubes. The carbonates were sprayed on treated nickel sleeves and baked for several hours in an electric oven. The coated sleeves were then mounted on a pressed seal together with grid and plate in the manner used in assembling the equipotential cathode type of radio tube, a slit being cut in the side of the plate so as to allow a beam of light to fall at normal incidence upon the cathode. The cathode lead wire was passed out through a bead on the top of the glass bulb in order to minimize leakage currents. For the emission measurements, grid and plate were joined together to form an anode. The value of the electric field at the cathode, calculated from the dimensions of cylindrical grid and cathode, is given by the relation $E=12.3V$ volts per centimeter, where V is the value of the applied potential in volts.

A small sized bulb was used, permitting the cathode to be brought close to the exit slit of the monochromator. The assembled tube was glass-sealed onto a mercury diffusion pump and baked in an electric oven for about one hour at 400°C. All metal parts were then brought to a yellow heat by means of an induction furnace, and the tube was pumped until all traces of gaseous discharge disappeared. The cathode was held at a red heat during this treatment and as a consequence the coating was partially activated at the termination of the degassing process. A combination magnesium-barium getter was flashed over the lower portion of the glass bulb, the tube then being sealed off the pump.

The bulb was placed in a light-tight box and mounted rigidly in such a position that beams of monochromatic light were completely intercepted by the coating of the cathode. The filament could now be heated and the cathode raised to various temperatures suitable for activating the coating. Tests on tubes prepared for these studies showed no gas ion currents measureable on a galvanometer having a sensitivity of 10^{-8} amperes when thermionic currents of from 10 to 20 milliamperes were drawn from the cathode.

Voltage supply and current measurement

Voltages were supplied by two power packs joined in series, each bridged with a 3000 ohm resistance having a variable contact. Thus, potentials ranging from one to one thousand volts were available for rapid measurement. Voltage readings were made on a Weston 1500 microammeter joined in series with two 500,000 ohm wire-wound resistances having zero temperature coefficient for the range used.

Photoelectric currents were measured on a high sensitivity Leeds and Northrup galvanometer having a resistance of about 900 ohms. Two different suspensions were employed during the course of the work, the current sensitivity in both cases being of the order of 10^{-11} amperes per scale division.

Monochromator

A 400-watt projection lamp was used as source of illumination. Light from one of the tungsten filament coils of this lamp was dispersed by a Van Cittert type double monochromator having glass prisms. Any desired band of the spectrum could be selected by moving the central slit, thus making it unnecessary to alter the adjustment of the last slit or to change the position of the cathode while measuring the emission at various wave-lengths. The instrument was calibrated over the range from 4000 to 14000 Angstroms with emission lines from rare gas spectra and the mercury arc. Slit widths of from one to three tenths of a millimeter were used in the course of the work. A slit width of 0.1 mm corresponds to a band 20A wide at 5000A, and to about 280A at the 12000A setting.

Operation

Leakage currents were largely avoided by sealing the cathode lead through the top of the bulb. A "zero" reading of the galvanometer was secured with no light falling on the cathode; then, by means of a shutter, radiation was admitted to the tube and a second reading taken, the process being repeated several times for each recorded observation. A slight decrease of photocurrents with time was noted for potentials in the neighborhood of 1000 volts. The galvanometer deflection recorded was that observed about ten seconds after the light beam was admitted. The energy of the radiation over the spectral region used was determined by means of a Moll microthermopile used in conjunction with a high sensitivity Leeds and Northrup galvanometer having a resistance of fifteen ohms.

Photo-Emission from Stock Cathodes

Preliminary measurements of the photoelectric activity of the cathodes in stock radio tubes of the '27 type illustrate the method used in this work. Light from the monochromator was allowed to fall through the top of the radio bulb and strike one side of the cathode at a glancing angle. It was impossible to avoid illuminating at the same time the cathode supporting wires, so the currents observed cannot be said to originate solely in the oxide coating. In many of the tubes leakage currents were of the same magnitude as the photocurrents obtained.

The results for ten such tubes are shown in Fig. 1. The plotted currents are the *total* emissions observed at each wave-length, and *not* the emissions per unit of radiant energy. The variation in amplitude of the emission is large, and there appears to be no correlation between total photo-emission and thermionic activity of these cathodes. Subsequent results obtained with tubes in which the light beam was directed solely upon the oxide cathode showed much smaller photo-currents, so it is evident that the large variation in amplitude of the currents obtained from the stock radio tube cathodes arises from the fact that the photo-activity observed is not merely that of the coating, but of coating plus activated cathode supporting leads.

One result is of importance. The long-wave limit as measured at a potential of 90 volts is sensibly constant, and falls at 10,400 ± 400A. The threshold of the sputtered cathode lead wires may be taken to be the same as that of the activated grid and plate in these tubes. This threshold had previously been measured and found to lie in the region from 7500 to 8500A; hence it is believed that *the long-wave limit at* 10,400A *is fixed by a photoelectric work-function which is characteristic of the oxide coating on the cathode.* This threshold may be corrected for the effect of the applied field by a method shown in a later section. When this is done, the zero field work function of this group of well activated cathodes is found to be 1.32 ± 0.05 volts.

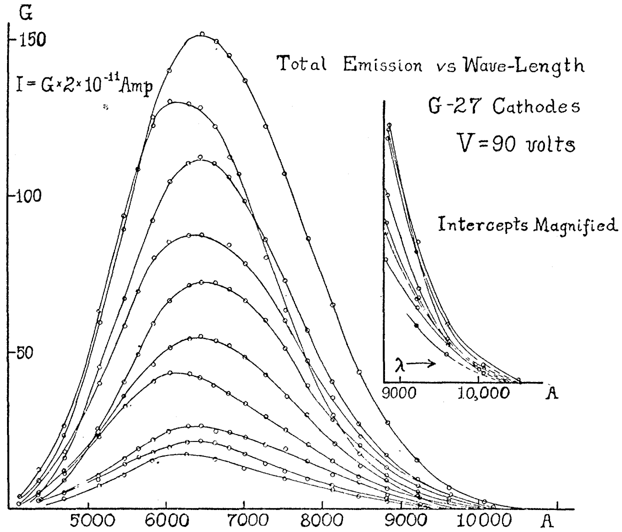

Fig. 1. Photoelectric currents obtained from the cathodes of '27, or heater type, radio receiving tubes.

VARIATION OF PHOTO-EMISSION WITH ACTIVATION

A study of the changes in surface structure which take place when the oxide is brought to an active state was made by obtaining the spectral sensitivity of the coating at each stage of the activation process. These tests were carried out with the specially prepared tubes in which the light beam was incident solely upon the coated portion of the cathode.

The treating-out process on the pump was carried to a point such that a few microamperes of thermionic current was obtained at normal cathode heating. After sealing off the tube and mounting it in front of the monochromator, usually no photo-emission could be detected. An activation treatment consisted in overheating the cathode for a few minutes, then dropping the filament voltage to normal value and noting the final steady value of thermionic current. When the tube was then cooled to room temperature, it was found that a completely stable and permanent value of photo-current at any given intensity of illumination could be obtained only after the tube had remained cold for a period of from 20 to 30 hours. Presumably this action is due to a slow clean-up of gas molecules by the free barium and strontium atoms in the surface of the coating. As previously noted, the tubes failed to show detectable gas-ion currents, indicating that the pressure was less than 10^{-7} mm of mercury.

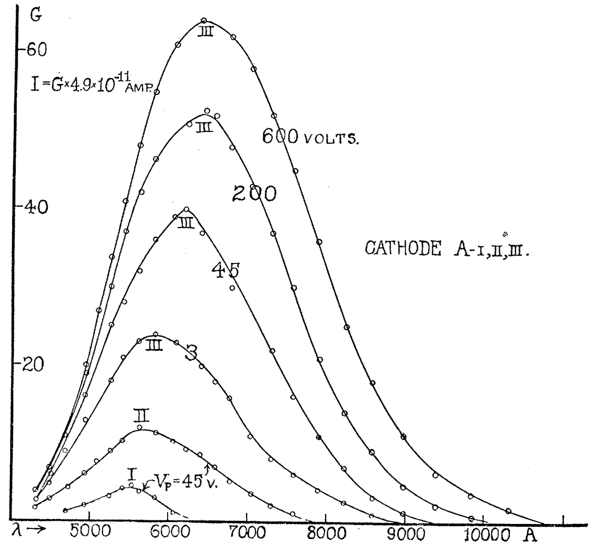

Fig. 2. Showing the variation in photo-emission with heat treatment of an oxide coated cathode.

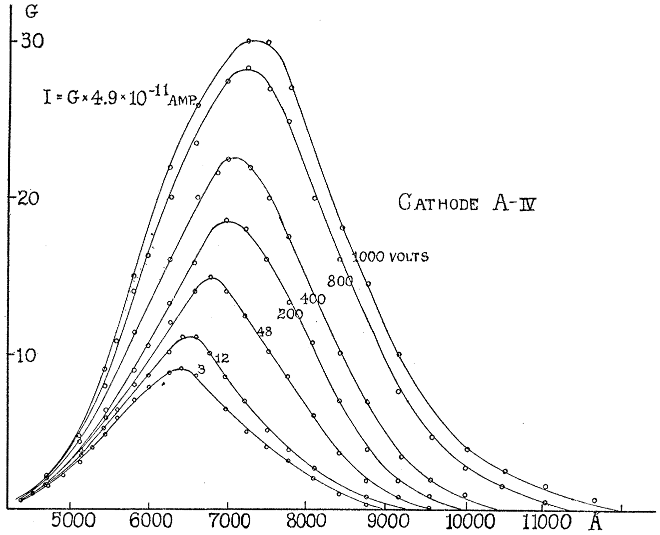

Fig. 3. Total photo-emissions from cathode A-IV, showing the effect of various accelerating potentials.

When a stable condition of photo-activity was obtained, current measurements were taken at various wave-lengths. The process was then repeated for several activations, until the thermionic tests indicated no further gain in emission. The data obtained for the first tube, designated as cathode *A*, are shown in the graphs of Fig. 2, which indicate clearly a shift of the long wave limit towards the red end of the spectrum as the activation is carried forward. Roman numerals refer to successive activations; the plot for activation IV is shown in Fig. 3 (48 volts anode potential), and the threshold frequency for activation V (not plotted) is $3.05\cdot10^{14}$ sec^{-1}, $\lambda_0=9830$A, as measured at a grid-plate potential of 45 volts. Similar results were obtained with other cathodes.

TABLE I. *Activation data, cathode A, anode potential, 22.5 volts. Surface temperature during thermionic tests, 1120°K.*

No.	Thermionic current in milliamp.	Thresholds for $V=45$ v.	Work function at zero field*
I	10.6	$4.68\cdot10^{14}$ sec^{-1}	2.00 volts
II	17.0	3.82	1.64
III	21.0	3.38	1.46
IV	24.2	3.13	1.36
V	30.0	3.05	1.32

* These values for the photoelectric work function are computed on the assumption that the effect of the field is the same for low and high activations.

Table I gives the values of thermionic currents obtained after each heat treatment for cathode *A*, the corresponding threshold frequencies at 45 volts anode potential, and the photoelectric work functions reduced to zero field. We shall have occasion to refer to these data in a later section dealing with thermionic properties of the coating.

SHIFT IN LONG WAVE LIMIT WITH APPLIED FIELD

Investigations in this laboratory of the maximum excursion of the long wave limit for pure barium films have revealed a noticeable dependence of the photoelectric threshold upon the applied field. The effect is particularly striking in the case of activated oxide cathodes. Figs. 2, 3 and 4 show plots of total photo-emission in terms of galvanometer deflections for two cathodes, *A* and *B*. The light source was maintained at a constant intensity throughout. With the anode at a given potential the wave-length of the monochromatic beam was varied over the spectral region and the mean galvanometer deflection obtained for each setting of the monochromator. It is to be noted that there is a progressive shift of the maxima in the total emission, and of the long wave limits, with change of applied potential.

Fig. 2 shows the effect of the applied field in the case of cathode *A*, activation III; Fig. 3, that for the same cathode when the activation was carried one step farther. At present no theory is advanced for the decrease in amplitude of the emission in the second case. It is probably due to a change in surface structure of the oxide. The amplitude decreased still more for activation V. Fig. 4 gives the results for cathode *B* following a second heat treatment.

Fig. 5 indicates the change in threshold frequencies with applied voltage for cathode *A*-IV. If these threshold frequencies, determined by extrapolation, are plotted against $E^{1/2}$, where E is the field in volts per centimeter at the cathode, the points fall nearly on a straight line. Such plots for cathodes *A* and *B* are shown in Fig. 6. This relation suggests a change in work function due to the neutralization of image forces at the surface of the cathode. Quantitatively the effect is much too large to be explained by Schottky's electron image theory for metal surfaces.

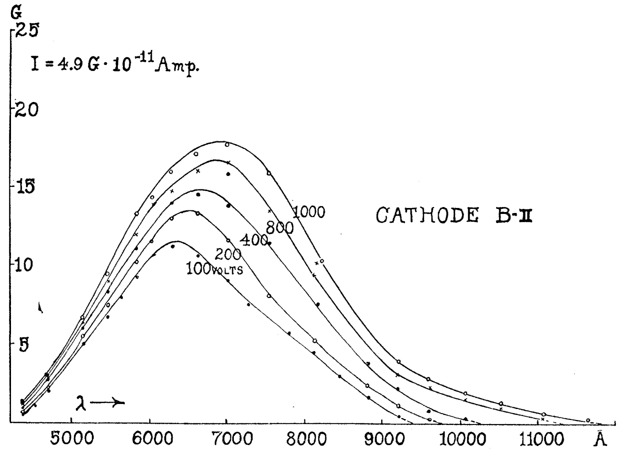

Fig. 4. Total photo-emission from cathode *B* after a second heat treatment, showing the effect of various accelerating potentials.

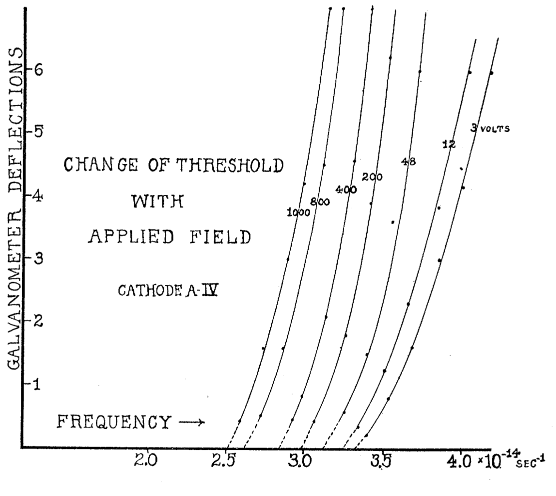

Fig. 5. The photo-currents, plotted to a large scale, as a function of frequency near the long-wave limit. Cathode *A*-IV.

In the present case it is inconceivable that light could penetrate through the thick coating and cause photoelectric emission from the core metal surface. Evidently the intrinsic fields which are modified by the applied field, resulting in a reduction of electron work function, are due to atoms and ions of barium (or of barium and strontium) adsorbed on the outermost layers of the oxide crystals.

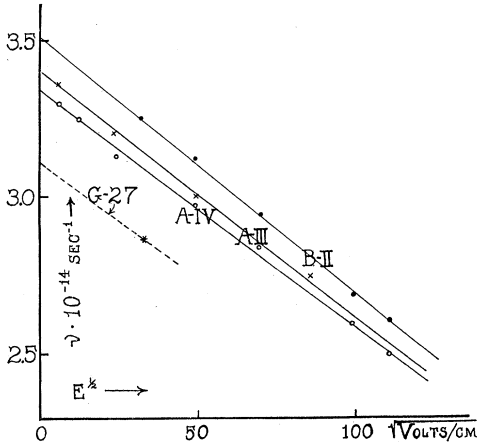

Fig. 6. Threshold frequencies, as determined by extrapolation from the type of plot illustrated in Fig. 5, are shown here plotted against the one-half power of the applied electric field. Results are shown for cathodes *A*-III, *A*-IV and *B*-II.

Comparison of Results with Theories of the Photoelectric Effect

From the plots of Figs. 2, 3 and 4 it is evident that the tendency to non-saturation of the photo-currents increases with the wave-length of incident radiation. This may also be shown by plotting the current as a function of the accelerating potential for different colors of light. An example of such a plot

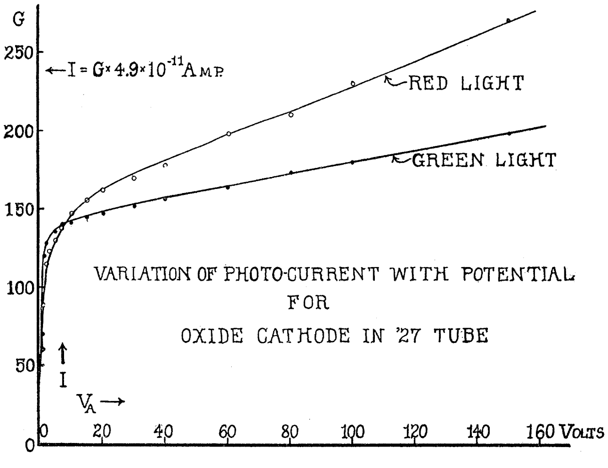

Fig. 7. Illustrating the condition of non-saturation in photo-currents from the oxide coated cathode of a stock radio tube, and dependence of the effect upon color of incident radiation. (Light intensities were adjusted to give the same photo-current at $V = 10$ volts.)

is illustrated in Fig. 7. The upper curve is for light from a tungsten filament focused upon the cathode of a radio tube, through a ruby glass filter; the lower curve is that obtained by using a sextant green filter.

The problem which now arises is that of determining whether or not the continued rise of current with increase of accelerating potential may be completely accounted for by a change in work function with applied field, or whether it may arise from other causes. Since the effect is dependent upon the color of light used to illuminate the emitting surface, a complete solution of the problem involves a knowledge of the dependence of emission on frequency of the incident radiation. In the discussion which follows, two theories of the photoelectric effect have been considered, one based on classical physics, the other on wave mechanics. It is assumed that the change in work function varies linearly with the one-half power of the field, and theoretical expressions are obtained giving the photo-current as a function of field and of light frequency. In order to determine which of the two equations more nearly represents the observed change of emission with field, plots are drawn up for comparison. A further test consists in calculating from the emission data the true, or zero-field, photoelectric work function of the emitting surface. When the wave-mechanical expression is used, the values are found to agree, within the limits of experimental error, with those obtained from a consideration of the long wave limits.

Compton-Richardson equation

Compton and Richardson[5] have developed an equation connecting the frequency and number of electrons emitted per unit time for light of unit intensity, of the form

$$i = k(\nu - \nu_0')/\nu^3 \tag{1}$$

where k is a constant for a given substance, ν the frequency of the incident light, and ν_0' the threshold frequency. If we assume that $\nu_0' = \nu_0 - aV^{1/2}$ is the value of the threshold for an applied field which is proportional to the accelerating potential V, we have by substitution in (1),

$$i = k(\nu - \nu_0 + aV^{1/2})/\nu^3, \tag{2}$$

in which ν_0 is the zero field threshold. Thus, when ν is held constant, i should vary linearly with the one-half power of the accelerating voltage. On the basis of observed emissions such a dependence does not satisfactorily account for the characteristic obtained. Moreover, quantitative agreement is lacking between the change in work function with applied field computed on the basis of this theory and the observed shift in the photoelectric threshold.

Houston equation

More recently theories have been developed for the dependence of photoemission upon frequency of the incident light, which are based upon wave mechanics and the newer statistical mechanics. The application of these theories to experimental results is discussed in detail in a paper by Lawrence and Linford,[6] who have measured the shift in photoelectric threshold with

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[5] K. T. Compton and O. W. Richardson, Phil. Mag. **26,** 549–567 (1913).

[6] E. O. Lawrence and L. B. Linford, Phys. Rev. **36,** 482–497 (1930).

applied field for thin potassium films on tungsten. These authors give an equation derived by Houston,[6'] and based upon the previous work of Wentzel, as follows:

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

where I is the photoelectric emission at 0°K, ν is the frequency of light having electric vectors proportional to E_x, E_y, E_z, incident on a metal surface with the normal along the x-direction, ν_0 is the threshold frequency, and $\bar{\epsilon}$ is the maximum energy of the electrons in the degenerate Fermi distribution.

Photoelectric sensitivity of the emitting surface

In order to compare the emission actually observed with that given by the above expression, considerable simplification of the equation is necessary. We consider first the variation of current with frequency of incident light, presuming the threshold to remain constant for a given applied field. If we assume a perfectly plane emitting surface, with light falling upon it at normal incidence, then $E_x=0$, and $\overline{E_y^2}=\overline{E_z^2}=$ a constant. Rewriting Eq. (3) so as to express I as a function of λ, and differentiating to determine the maximum in the sensitivity curve, $I_{\max}$ falls at $\lambda_{\max}=\lambda_0/3$. For the Compton-Richardson equation, $\lambda_{\max}=2\lambda_0/3$, in which λ_0 is the long wave limit. Plotting the observed current per unit radiant energy against wave-length, the maxima in the emissions obtained from well-activated cathodes is found to lie between these two values.

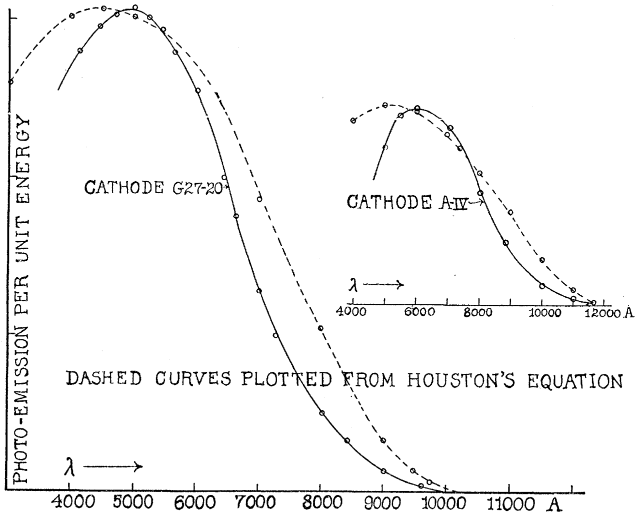

Fig. 8. Comparison of the theoretical and observed photo-sensitivities of oxide cathode emitters

It is of interest to calculate approximately where the theoretical maximum sensitivity should occur if the light does not fall at normal incidence. The oxide surface is actually not smooth, but consists of elementary crystal sur-

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[6'] Reference 6, p. 495.

faces oriented at all possible angles with respect to the direction of propagation of the incident radiation. If we may assume that in general $\overline{E_x^2}=\overline{E_y^2}=\overline{E_z^2}=$ a constant for the mean square values of components of the electric vector, then the maximum is found to lie between the limits $\lambda_{\max}=\lambda_0/3$, and $\lambda_{\max}=2\lambda_0/3$. The resulting equation is too complex to permit a direct determination of $\lambda_{\max}$ without a great deal of labor. The easiest method of comparing theoretical and experimental results is to plot the current per unit of energy for each case, adjusting the calculated values of I so that $I=0$ for $\lambda=\lambda_0$, and has the same value at the maximum as that shown in the experimental plot. The value assigned to $\bar{\epsilon}$ does not greatly affect the result; in the present computations $\bar{\epsilon}$ has been taken as 2.4 electron-volts, assuming that barium atoms constitute the emission centers.

Such plots are shown in Fig. 8 for the case of two cathodes that gave sufficient emission at the short wave-lengths to permit fairly accurate determinations of the observed maxima. In all cases it was found that the observed maxima occurred at longer wave-lengths than those predicted by the Houston equation. Unfortunately, in the present work, the sensitivity plots for the observed emission are least accurate in the region from 4000 to 5000A, since at this end of the spectrum both the photo-currents and the e.m.f. generated in the microthermopile are small in value, and cannot be determined with great precision. In general, Eq. (3) represents the photosensitivity of the oxide cathodes more closely than does Eq. (1).

Zero-field thresholds

Only an approximate theoretical calculation of the effect of applied fields upon the photoelectric emission is attempted in this paper. For this, simply the case in which we may assume that the light falls at normal incidence upon the cathode surface is considered in the simplification of Eq. (3). Then $E_x=0$, $\overline{E_y^2}=\overline{E_z^2}=$ a constant, and Eq. (3) takes the form

$$I = k^3(\nu-\nu_0')^3/\nu^{9/2} \tag{4}$$

in which k is a constant and ν_0' is the effective threshold frequency. Supposing there are surface fields such that

$$\nu_0' = \nu_0 - bE^{1/2}$$

expresses the dependence of the threshold upon the applied field, E, we have, by substitution in (4),

$$I = [k^3\nu^{-9/2}](\nu-\nu_0+bE^{1/2})^3 \tag{5}$$

in which ν_0 is the value of the threshold at zero applied field, and this, as well as the proportionality factors b and k, are constants still to be determined by comparison with experimental results.

How well Eq. (5) expresses the dependence of the current upon applied field may be determined by plotting $I^{1/3}$ against $E^{1/2}$ (or $I^{1/3}$ against $V^{1/2}$, where V is the accelerating potential). For a given color of illumination (constant ν) the graphs should be straight lines. Fig. 9b, c, d, shows such plots for cathodes *A*III, *A*IV, and *B*II. The emission values are taken from the graphs of Figs. 2, 3 and 4, the color and intensity of the light being constant for each plot. Obviously it is not necessary to reduce the observations to photoemission per unit light intensity. Except for values of accelerating potential less than about 50 volts, the plotted points fall approximately on straight lines.

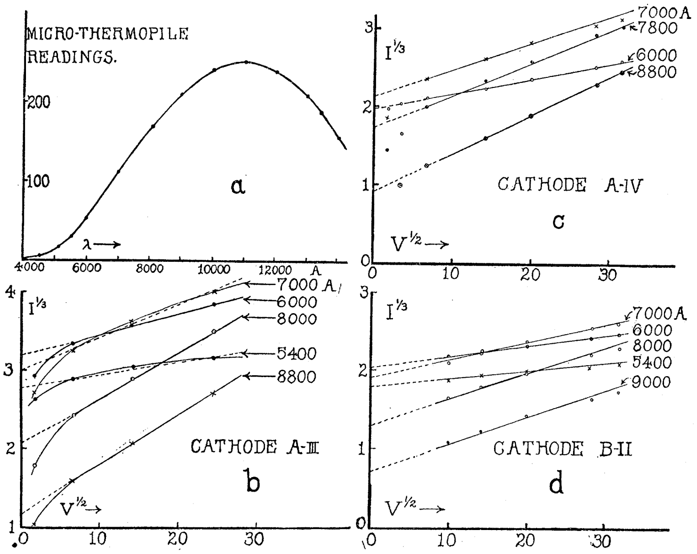

Fig. 9. (a) Microthermopile readings plotted against wave-lengths, VanCittert monochromator, using hot tungsten filament source. (b), (c), (d) $I^{1/3}$ vs $V^{1/2}$ plots for testing Eq. (5), and for determining zero-voltage "saturation" current values.

If the line which passes through most of the points be extended back until it cuts the axis of ordinates, the value of $I_0^{1/3}$ may be obtained which corresponds, for a given frequency of illumination, to the current which would result with zero applied field, were it possible to eliminate all effects of electron space charge. At zero potential, $\nu_0' = \nu_0$, and from Eq. (4) we have,

$$I_0^{1/3} = k(\nu - \nu_0)/\nu^{3/2} \text{ or } k = \frac{I_0^{1/3}\nu^{3/2}}{(\nu - \nu_0)} \cdot \tag{6}$$

Substituting this value of k in Eq. (4) we obtain

$$(I/I_0)^{1/3} = \left(\frac{\nu - \nu_0'}{\nu - \nu_0}\right) \tag{7}$$

Eq. (7) expresses how the current I should change from its saturation value I_0, at zero field, as the effective threshold, ν_0', varies in value, when the color of the incident light is held constant. How well this equation represents observed results might be tested by using values of ν_0' and ν_0 obtained independently from considerations of the long wave limits for a given surface. This has been done and the observed changes in emission differ in magnitude from those predicted by some 15 or 20 percent.

Another mode of procedure is to obtain values for the true threshold, ν_0, directly from Eq. (7) by equating the expressions for ν_0', corresponding to a given field, for two light frequencies, ν and ν'. Thus, omitting the intermediate steps,

$$\nu - (\nu - \nu_0)(I/I_0)^{1/3} = \nu' - (\nu' - \nu_0)(I'/I_0')^{1/3}$$

in which the primed quantities are the currents and frequency for a second color of illuminating radiation. Setting $r=(I/I_0)^{1/3}$, and $r'=(I'/I'_0)^{1/3}$, and solving for ν_0 we obtain,

$$\nu_0 = \frac{\nu'(r' - 1) - \nu(r - 1)}{r' - r} \cdot \tag{8}$$

Table II shows the results of calculations of the zero field thresholds for three cathodes, following the method outlined above. Values of current ratios, r and r', were chosen in the range from 45 to 1000 volts anode potential. Each value of threshold shown represents the average of from 20 to 30 ν_0's calculated by using various pairs of frequency values, at various anode potentials. The maximum fluctuation from the mean is about 20 percent. Large variations may be expected, since the results depend critically upon the slopes of the lines of Fig. 9 from which the I_0's are obtained. These calculated values of zero field threshold fall below those obtained from the long wave limits (Fig. 6), but in general the agreement is satisfactory.

TABLE II. *Zero field thresholds calculated from the equation,* $\nu_0 = \dfrac{\nu'(r'-1)-\nu(r-1)}{(r'-r)}$.

	Voltage range	Range of frequencies	Average values ν_0	ν_0 from long-wave limits
Cathode *A* III	45– 600	3.75–$5.56\cdot 10^{14}$	$3.14\cdot 10^{14}$	$3.40\cdot 10^{14}\,\mathrm{sec}^{-1}$
Cathode *A* IV	48–1000	3.40–5.00	3.12	3.34
Cathode *B* II	100–1000	3.33–5.00	3.11	3.51

That one may arrive at even an approximate value of the zero field threshold of a surface from calculations based on current—potential plots and a knowledge of the frequency of the incident light, lends weight to the hypothesis that the lack of saturation in the observed photo-currents is caused by a lowering of the work function with increase of applied field. Furthermore, it appears that the form of the dependence of emission upon frequency is that given by Houston's equation. It is obvious that an attempt to apply this method to ordinary metal surfaces would fail, since the shift in threshold is small up to values of electric field which would give rise to auto-electronic currents. It should be possible, however, to apply these calculations to the changes observed with thin alkali metal films under the action of fields of the order of 10,000 to 100,000 volts per centimeter.

THERMIONIC PROPERTIES OF OXIDE CATHODES

In the course of the present investigation no extensive study of thermionic emission was undertaken. A few observations carried out at low cathode heating, and calculations based on activation tests, indicate that probably the thermionic and photoelectric work functions for these surfaces have the same value.

Thermionic work function at low temperatures

Near the close of the investigation one set of observations was taken at low temperatures to determine the Richardson line for one cathode. It is to be noted here that there are several advantages to be gained in working at low temperatures: thermionic and photoelectric emissions may be obtained under nearly the same temperature conditions with little danger of altering the surface structure of the coating by heating, and much higher potentials may be applied than at normal cathode heating. Using cathode BII it was found that the log i vs $V^{1/2}$ plots gave straight lines for potentials in excess of 40 volts, up to 1000 volts, over the temperature range from 370° to 530°K. It was thus possible to obtain values of the emission current at zero field for each temperature by extrapolation. The thermionic work function determined in this manner was 1.42 volts, corresponding to the zero field photoelectric value of 1.44 volts for the same surface (see Fig. 6). The agreement is well within the limits of experimental error.

Variation of ϕ and A with activation

Values of the thermionic currents measured at the same temperature for various stages of activation of cathode A are shown in Table I. If, for each stage, we take the thermionic work function to be identical with the zero field photoelectric value, and assume A constant, then the temperature required by the Richardson-Dushman equation,

$$i = AT^2e^{-b/T}, \tag{9}$$

is in the neighborhood of 10,000°K. The surface temperature measured by means of an optical pyrometer was 1120°K. Either, with constant value of A, the change in thermionic work function is very small, (of the order of 0.15 volt) or both A and b change with activation. We have reason to believe from the reports of other investigators on the work function of oxide coatings, that the latter is probably the case.

Espe[7] observed that while b remained fairly constant for a strontium oxide coating during activation, A increased considerably. Detels,[8] who measured the thermionic work function for various activations of barium-strontium coatings on nickel, found that both A and b decreased during activation, and that the decrease in log A was approximately proportional to that in b.

TABLE III. *Variation of A and ϕ with activation. Cathode A, heat treatments I to V. Normal test temperature = 1120°K.*

No.	i/cm^2	ϕ	A	ϕ*	A*	Values given by Detels ϕ	 A
I	0.0141 amp.	1.93	44.8	2.00	59.8	2.37	27.5 amp/cm^2 T^2
II	0.0227	1.57	.24	1.64	0.435	1.83	1.24
III	0.0280	1.39	.040	1.46	0.049	1.36	0.0373
IV	0.0322	1.29	.016	1.36	0.0207	1.36	0.0297
V	0.0400	1.24	.0116	1.31	0.0141		

* Values of ϕ and A corresponding to zero accelerating field, assuming that the variation of work function with field is not a function of the temperature. Work functions are in volts.

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[7] S. Dushman, Rev. of Modern Physics **2,** 436–37 (1930).

[8] F. Detels, Jahrb. d. drathlos. Telegr. **30,** 10, 52 (1927).

Calculations based on the activation data for cathode A, assuming the photoelectric and thermionic work functions to be identical, are shown in Table III. The approximate area of the emitting surface is 0.75 cm^2, and the activation test temperature is taken as 1120°K. Fig. 10 shows plots of log A vs ϕ for values given by Detels and for our results. The plots nearly coincide at the higher activations. That this is more than a chance agreement is indicated by the fact that both sets of results are for barium-strontium oxide coated nickel. Moreover, our values of A are probably too high at the lower activations. The thermionic currents were measured at 22.5 volts anode potential, and it is difficult if not impossible to obtain current values extrapolated to zero field at normal cathode heating. At the lower activations the emission saturates poorly, and the current values are therefore too high. As the cathode becomes activated, however, the currents exhibit better saturation, and the values obtained at III, IV and V (Fig. 10) are therefore much closer approximations to the currents which would be obtained with no accelerating field. It is believed that these results indicate a close agreement in the values of the two work functions, and show that the thermionic and photoelectric electrons originate in the same layer of adsorbed atoms.

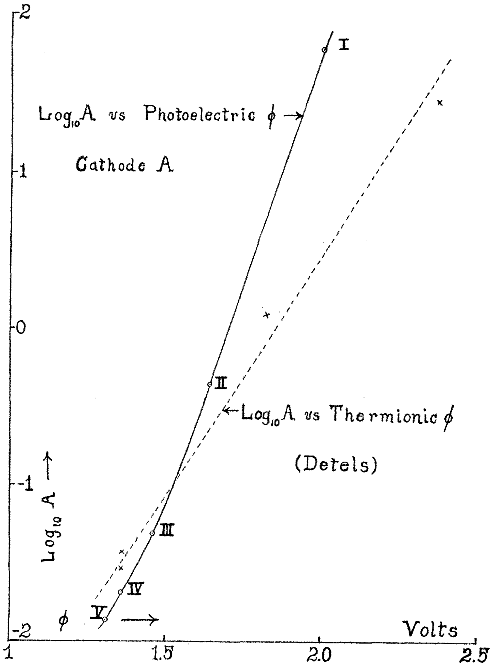

Fig. 10. The solid line represents the observed change of log A (for the thermionic emission) with photoelectric work function, ϕ, during activation of cathode A. The other points are taken from data on oxide cathodes published by Detels, for which now the values of ϕ are measured thermionic work functions, in volts.

These results are in qualitative agreement with those obtained by Becker and Mueller[9] for caesium films on tungsten, and for thoriated tungsten. These

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[9] J. A. Becker and D. W. Mueller, Phys. Rev. **31**, 431–440 (1928).

investigators show that for a complete monatomic layer of caesium the currents approach metallic saturation. Also that for the log i vs $E^{1/2}$ plots, a linear relation is not found for the lower values of electric field.

In addition, it is evident from the present work that the change in work function caused by the applied field depends upon the temperature of the cathode, since our results show a continuously decreasing slope in these plots as the temperature is raised, in the case of thermionic measurements carried out at low cathode heating where anode potentials up to 1000 volts could be applied.

SUMMARY OF RESULTS

That during the activation of an oxide cathode a photoactive surface film is formed whose work function decreases with heat treatment of the coating, is proven by the measurements described in this paper. This film, which is probably composed of barium atoms, has properties very similar to those of adsorbed films of the alkali metals. The formation process in the case of the oxides, however, is complicated by the simultaneous release of elements other than barium and strontium which are given off while the coating material is being decomposed. The photoelectric threshold shifts to longer wave-lengths as the applied field is increased, in a manner similar to that observed in the case of adsorbed alkali films. A preliminary study of thermionic properties of the coating shows that both A and ϕ decrease in value during activation.

Results obtained in the present study tend to confirm the theory that lack of saturation observed in photoelectric emission at room temperature, and in thermionic currents obtained at low cathode heating, is due to a decrease in work function with increase of accelerating potential. This contention is supported by the satisfactory agreement found between values of zero field thresholds obtained from the ν_0 vs $E^{1/2}$ plots, and those independently calculated from the observed variation of emission with applied field. For this calculation use was made of an equation recently developed by Houston for the dependence of photoelectric current per unit of radiant energy upon the frequency of incident light and the effective threshold. From the log i vs $E^{1/2}$ plots of the thermionic emission it is apparent that the applied field causes a smaller change in thermionic work function the higher the temperature.

Measurements at low temperatures of the thermionic currents from one cathode indicate good agreement between the zero field work function and the corresponding photoelectric value obtained from the long wave limits. This evidence, as well as the close agreement between the observed photoelectric work functions at various activations and the thermionic work functions for similar coatings obtained by other investigators, indicates that in both types of currents the electrons are emitted from areas of low work function which exist in the outermost surface layers of the oxide, rather than from activated layers on the surface of the core metal.

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