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An Investigation of Short-Time Thermionic Emission from Oxide-Coated Cathodes

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Vacuum-tube circuits were developed to measure thermionic current as a function of time for times ranging from 0.2 to 300 μsec. The decay with time of the temperature-saturated electron emission from oxide-coated cathodes was observed with this apparatus. Simultaneously with the application of anode voltage to an experimental diode the thermionic current density rose to an initial value and subsequently decayed to a steady value 1/5 to 1/15 of the initial value. The rate of decay was proportional to the current density, the decay requiring about 20 μsec. at 1200°K and about 500 μsec. at 900°K. The initial current exhibited a somewhat greater anode-voltage effect than did the steady-state current. The range of decay was independent of the thickness of cathode coating over the region 1 to 30 mg of oxide per cm^2. An electrolytic conduction hypothesis of the decay process is proposed. The form of the observed current as a function of time agreed with the form predicted by this theory. The observed rate of decay, as interpreted on the basis of the electrolytic conduction hypothesis, indicated that within a single crystal of barium or strontium oxide between 0.05 and 0.5 of the total conduction current is ionic. The possible connection of this decay and the "flicker effect" is noted.

I. INTRODUCTION

ALTHOUGH the first oxide-coated cathode was prepared forty years ago, knowledge of the process of thermionic emission from such cathodes is still in a very unsatisfactory state. Recently, experimenters have applied to these emitters periodic fields such that current was drawn during a pulse of a few μsec. duration and no current was drawn for the rest of a period. It was discovered that the average temperature-saturated current during each pulse was considerably greater than the current which could be emitted continuously by the same cathode under the same conditions of temperature and electric field. The present work was directed toward finding the decay characteristics of oxide cathodes, and the dependence of the decay time and the maximum current on temperature and on the chemical properties of the cathode coatings. There was a threefold purpose for this investigation: First, knowledge of the decay characteristics would enable one more confidently and efficiently to design cathodes for delivering current intermittently. Second, any increase in our knowledge of the emission process from oxides which might result from such an investigation would be very welcome. Third, it might happen as a result of this work that, by suitable changes in cathode material, thickness, or core metal, the initial (maximum) current could be drawn for a longer time or, perhaps, continuously.

II. APPARATUS

The experimental tubes used in this investigation were "sealed-off," high vacuum diodes. Anodes were nickel blocks drilled to provide a 0.32-cm diameter hole for the anode surface; a small peep-hole was provided in the anode, so that an optical pyrometer could be focused on the emitting surface of the cathode. Cathode sleeves were 0.127-cm diameter tubes of nickel containing 0.2 percent silicon. The sleeves were hydrogen-fired and then sprayed with alkaline-earth carbonate mixtures suspended in amyl acetate. Each cathode was trimmed to the required emitting area (about 0.05 cm^2) by scraping away the undesired part of the coating and polishing the underlying nickel. Tests on cathodes of widely different trimmed areas showed that the nickel from which carbonates had been removed exhibited the thermionic electron emission characteristic of pure nickel.

A cathode and anode were assembled into a tube and aligned concentrically with mica spacers. A rigorous heat treatment was employed during the exhaust of each tube in order to outgas all parts. Cathodes were activated by glowing at

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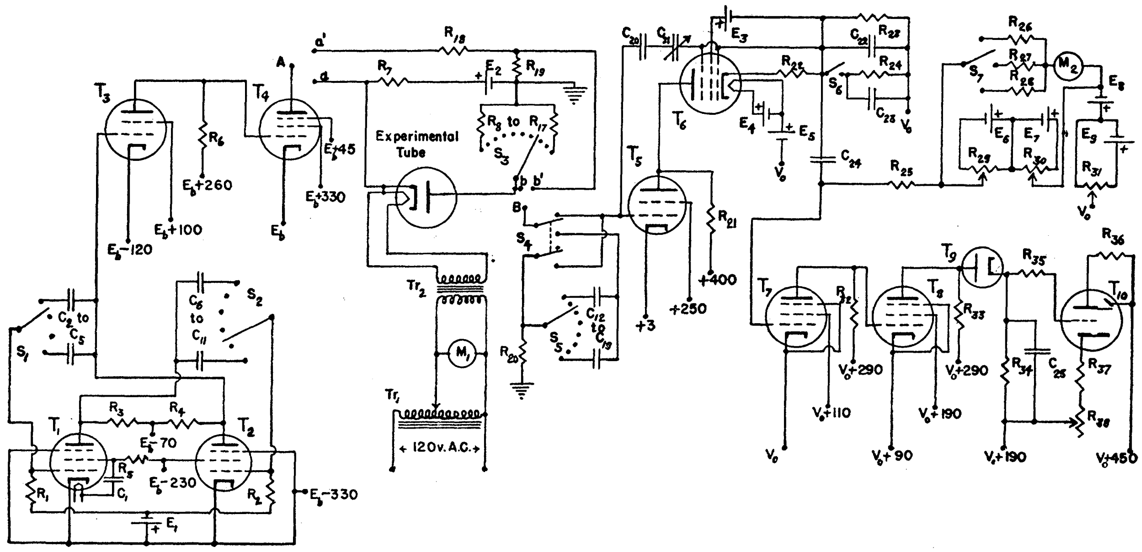

FIG. 1. Square wave generator, experimental tube, and pulse measuring circuits.

$T_1, T_2, T_7 \rightarrow 6C6$.
$T_3 \rightarrow 6L6$.
$T_4 \rightarrow 804$.
$T_5 \rightarrow 6L6G$.
$T_6 \rightarrow 6J7$.
$T_8 \rightarrow 6D6$.
$T_9 \rightarrow 6H6GT$ (one diode).
$T_{10} \rightarrow 6E5$.

$C_1 \rightarrow 16$ μf elect.
$C_2, C_7 \rightarrow .0005$ μf.
$C_3, C_8, C_{24} \rightarrow .001$ μf.
$C_4 \rightarrow 0.003$ μf.
$C_5, C_9, C_{22} \rightarrow .005$ μf.
$C_6 \rightarrow 0.0002$ μf.
$C_{10} \rightarrow 0.01$ μf.
$C_{11} \rightarrow 0.02$ μf.
$C_{12} \rightarrow 58$ μμf.
$C_{13} \rightarrow 100$ μμf.
$C_{14} \rightarrow 245$ μμf.
$C_{15} \rightarrow 555$ μμf.
$C_{16} \rightarrow 890$ μμf.

$C_{17} \rightarrow 0.00211$ μf.
$C_{18} \rightarrow 0.00527$ μf.
$C_{19} \rightarrow 0.0112$ μf.
$C_{20} \rightarrow 40$ μμf.
$C_{21} \rightarrow 20\text{–}80$ μμf.
$C_{23} \rightarrow 0.03$ μf mica.
$C_{25} \rightarrow 0.05$ μf.

$Tr_1 \rightarrow 2$ Kva. Variac.
$Tr_2 \rightarrow$ Filament transformer, rewound.

$M_1 \rightarrow 0\text{–}150$ volt a.c.
$M_2 \rightarrow 0\text{–}200$ μamp.
$S_1, S_2, S_3, S_5 \rightarrow$ tap switches.
$S_4 \rightarrow DPDT$, low capacity.
$S_6 \rightarrow SPST$, time sensitivity selector.
$S_7 \rightarrow SP3T$, range selector for M_2 used as voltmeter.

$E_1, E_7, E_9 \rightarrow 1.5$ v.
$E_2, E_4 \rightarrow 6$ v.
$E_3 \rightarrow 45$ v.
$E_5 \rightarrow 23$ v.
$E_6, E_8 \rightarrow 4.5$ v.
$E_b, V_0 \rightarrow$ see text.

$R_1 \rightarrow 300K$.
$R_2, R_{34} \rightarrow 2M$.
$R_3 \rightarrow 25K$.
$R_4 \rightarrow 15K$.
$R_5, R_{37} \rightarrow 1K$.
$R_6 \rightarrow 3.5K$, 50 watt.
$R_7 \rightarrow 175K$.
$R_8 \rightarrow 38.7$.
$R_9 \rightarrow 49.4$.
$R_{10} \rightarrow 75.7$.
$R_{11} \rightarrow 100.3$.
$R_{12} \rightarrow 153.1$.
$R_{13} \rightarrow 193$.
$R_{14} \rightarrow 304$.
$R_{15} \rightarrow 507$.

$R_{16} \rightarrow 1.24K$.
$R_{17} \rightarrow 1.83K$.
$R_{18} \rightarrow 2.5K$, 4 watt.
$R_{19} \rightarrow 75$.
$R_{20} \rightarrow 4.92K$.
$R_{21} \rightarrow 2.5K$, MPO 50 watt non-inductive.
$R_{22} \rightarrow 2K$.
$R_{23} \rightarrow 500K$.
$R_{24} \rightarrow 75K$.
$R_{25} \rightarrow 20M$.
$R_{26} \rightarrow 1.5K$.
$R_{27} \rightarrow 6K$.
$R_{28} \rightarrow 30K$.
$R_{29} \rightarrow 25K$ pot.
$R_{30} \rightarrow 5K$ pot.
$R_{31} \rightarrow 1K$ pot.
$R_{32} \rightarrow 250K$.
$R_{33} \rightarrow 50K$.
$R_{35} \rightarrow 150K$.
$R_{36} \rightarrow 750K$.
$R_{38} \rightarrow 1K$ pot.

Condensers above 0.01 μf are paper, 0.01 μf and below are mica, unless otherwise noted; $K = 1000\Omega$; $M = 1{,}000{,}000\Omega$; Resistors are 1 watt unless otherwise noted.

1300°K and slowly applying a potential difference between anode and cathode. A nickel-clad barium getter was flashed in each tube, and the tube sealed from the pumping system at a station pressure of less than 10^{-6} mm of mercury.

The requirements for an instrument with which to investigate the time effect under consideration were: (1) An electric field must be applied to the cathode surface in such a manner that the thermionic current increases from zero to a temperature-limited value in a time short compared to one μsec.; (2) after a short interval, this field must be removed, in order to allow time for the cathode to recover; (3) the current *vs.* time characteristic of a cathode must be faithfully reproduced, even when the current peaks are of only a few μsec. duration; (4) current pulses differing by a factor of fifty or more in amplitude and in decay time must be accessible, in order to ascertain the temperature dependence of the effect. Further requirements were imposed by the impossibility of procuring at the present time certain tubes, notably thyratrons, transmitting tubes, and high transconductance amplifying tubes.

The vacuum tube circuits developed to meet these requirements are outlined in Fig. 1. Tubes T_1, T_2, T_3, and their adjacent circuits constitute a square wave generator which delivers positive pulses to T_4. The width of these pulses can be selected by S_1 (about 100, 300, 600, or 2000 μsec.) and the pulse repetition frequency can be selected by S_2 (about 20, 30, 60, 120, 600, or 1500 pulses per second). Condenser C_1 synchronizes

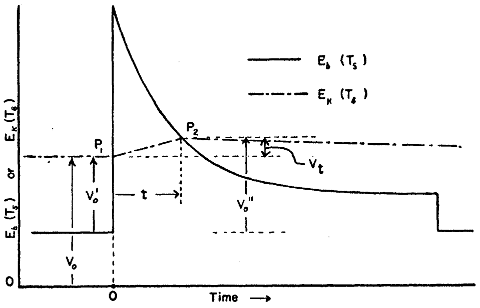

FIG. 2. Method of measuring current *vs.* time characteristics.

the pulses with the 60-cycle power line in order to minimize the effects of ripple and pick-up in the subsequent circuits. The control grid of T_4, which is about 70 volts negative with respect to T_4 cathode during most of a cycle, is driven positive for the duration of the pulse. The potential E_b (less the small drop across T_4) is applied suddenly to the experimental tube, if "*A*" is connected to "*a*:" The value of E_b ranges from -100 to -1000 volts, depending on the plate voltage desired at the experimental tube. The function of E_2 and R_7 is to apply a small negative potential to the plate of the experimental tube during the (major) fraction of the cycle in which T_4 conducts only a few microamperes. The transformer Tr_2 is specially constructed to minimize the capacitance between secondary and ground. The entire capacitance which must be charged through T_4 is less than 30 $\mu\mu$f, which permits applying a potential difference of 500 volts to the experimental tube in about 0.05 μsec.

The remainder of the circuits serve to measure the size and shape of the current pulse in the experimental tube. Switch S_3 selects an appropriate resistance so that the potential drop between ground and the point "*B*" will be about 15 or 20 volts at the maximum of the current pulse. With "*B*" connected to "*b*" and S_4 in the upper position, a negative pulse is applied to the grid of T_5. This pulse is mirrored in the plate circuit of T_5 and subsequently measured. With "*A*" connected to "*a*′," and "*B*" to "*b*′," a negative square wave is applied to "*B*." If S_4 is in the lower position, the resistance-capacitance combination of R_{20} and one of the condensers C_{12} to C_{19} serves to apply an exponential (negative) pulse to the T_5 control grid. The values of R_{20} and of these condensers can be determined by bridge measurements, and hence a calibrating pulse of known shape and time constant can be applied to the measuring circuit. (The resistors used had negligible skin effect at frequencies less than 2 Mc).

The performance of T_6 approximates a diode in which the current passed is zero whenever the plate is negative with respect to the cathode and is a fixed value for any positive plate potential. Figure 2 shows the principle of measurement by use of such an ideal circuit element. The solid line shows the plate potential E_b of T_5 as a function of time; E_b rises abruptly from its quiescent value when the pulse arrives, then decreases. When E_b rises above the value of V_0 (approximate quiescent cathode potential of T_6), T_6 begins to conduct, charging C_{22}. The cathode potential of T_6 (dashed line in Fig. 2) rises slowly until E_b falls to P_2, at which point T_6 ceases to conduct. The T_6 cathode potential then slowly decreases (time constant of R_{23} and C_{22} is 0.0025 sec.) to V_0 again in preparation for the arrival of another pulse. The amplitude V_t of the cathode potential's excursion from V_0 is a measure of the time *t* elapsed between P_1 and P_2. By setting V_0 at successively different values and measuring the time *t* corresponding to each, a plot of V_0'' *vs.* *t* reconstructs the shape and size of the experimental tube current pulse. Closing S_6 introduces a larger condenser to be charged (but about the same time constant) and hence decreases the time sensitivity of the instrument.

Of course, T_6 is not such an ideal circuit element as assumed above, but because of its low screen potential and the cathode bias resistor R_{22}, T_6 forms a fairly good approximation to the ideal diode. Figure 3 shows the static characteristic of this tube in the circuit in which it is used. The deviation of this characteristic from ideal is im-

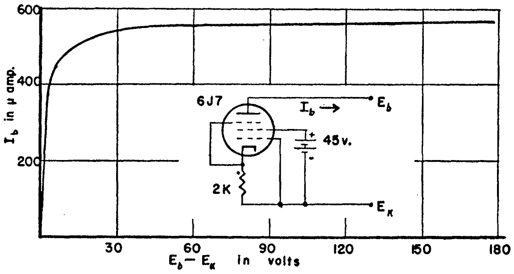

FIG. 3. Static characteristic.

portant only when examining a current pulse in a region where curvature of the current *vs.* time relation is large.

As E_b rises abruptly, a displacement current flows through T_6. In order to neutralize this, a simultaneous current pulse of opposite sign is applied by condensers C_{20} and C_{21}; C_{21} is adjusted to produce a minimum net effect of displacement currents.

The circuit beyond T_6 is merely a very sensitive vacuum tube voltmeter of the peak, slideback type; its function is to measure the amplitude V_t of the pulse generated by T_6 and its associated circuit. T_7 and T_8 are direct-coupled amplifiers; T_9 operates to increase the time constant of the pulse being measured from 0.0025 sec. to 0.1 sec. T_{10}, an eye type indicator tube, gives a visual indication when the balance point of the voltmeter has been reached. The network connecting R_{25} to V_0 is, of course, the control grid bias of T_7. When no pulses are applied to T_7, R_{31} is adjusted so that T_{10} shows the existence of a balance. When pulses are applied, the potential increment V_t which must appear across R_{29} and R_{30} to restore T_{10} to balance is a measure of the height V_t of the pulse and hence of the time during which T_6 was conducting. Switch S_7 selects the sensitivity of meter M_2, which measures V_t; the maximum sensitivity is 0.3 volt full scale, which allows measurement to 0.001 volt. Pulse amplitudes less than 0.2 volt can be measured to within 0.002 volt with this circuit; E_6 and E_7 total 6 volts, thus permitting measurement of pulses up to 6 volts in amplitude. An oscilloscope, connected from plate to cathode of T_7, serves as a monitor of the circuit operation.

Power supplies, various coarse and fine controls, and filter and by-pass condensers are not shown in Fig. 1. Voltage regulation is obviously important in the supplies for the direct-coupled amplifier, for the adjustable voltage V_0, and for the plate voltage of T_5. Since constant alternating current voltage was also needed for the heater of the experimental tube, the alternating current supply for all power supplies was taken from a motor-generator set with electronically regulated output voltage. In addition, all power supplies were electronically regulated.

Only the linear region of T_5 was used. The voltage gain of this circuit was measured in the usual manner, with precautions to insure that the screen grid potential during the measurements was the same as it was in actual operation. A meter circuit was devised which measured V_0' directly, the zero of this meter being set at the quiescent plate potential of T_5 (this circuit is not shown in Fig. 1).

The method for calibrating this instrument has already been outlined. If the circuit operates properly, V_t will be proportional to the time t elapsed from the beginning of the calibrating pulse, and we may write $t = CV_t$. Since the calibrating pulse is exponential with the time constant τ, we know that

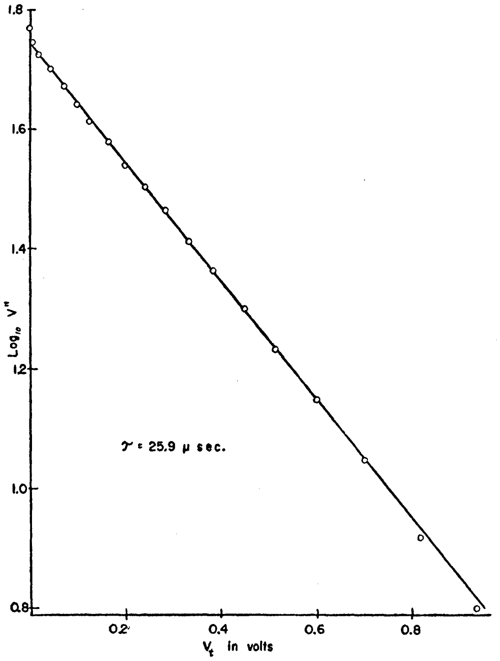

FIG. 4. Calibrating pulse.

$$V_0'' = (\text{constant}) \exp(-t/\tau). \tag{1}$$

A plot of $\log_{10} V_0''$ *vs.* V_t should then yield a straight line of slope m, where

$$m = (\Delta \log_{10} V_0'')/(\Delta V_t) = -C/(2.303\tau). \tag{2}$$

Figure 4 shows such a plot for $\tau = 25.9$ μsec., with S_6 closed (that is, low sensitivity to time); the points lie on a line, except for two points toward the "tail" of the pulse. The slope is evidently $m = -0.995$ per volt, and hence

$$C = -2.303\tau m = 59.5\ \mu\text{sec./volt}. \tag{3}$$

Calibrations were made for several pulses differing widely in time constant, and a calibration was taken each time the instrument was used. All calibrations were within 2 percent of $t=60V_t$ μsec. for the low sensitivity (S_6 closed) and within 4 percent of $t=9.5V_t$ μsec. for the high sensitivity (S_6 open).

The fidelity with which the instrument reproduces pulses of small time constant (of the order of several μsec.) and the rapidity with which the square wave rises must also be determined. In order to accomplish this, exponential pulses of time constants ranging from 2.5 to 50 μsec. were applied to the grid of T_5. The amplitudes of these pulses were equal at the grid, but unequal at the plate of T_5; the amplitudes at the plate were compared by using the voltmeter circuits as usual. Analysis of the circuit associated with T_5 enables one to determine the time constant of the T_5 plate circuit from these data. By this method the time constant of the T_5 plate circuit was found to be about 0.07 μsec.

The time constant of the rise of the square wave generated by T_4 could not be measured directly in this way. It can be inferred, however, that this time constant was less than 0.05 μsec. by two considerations: First, a comparison of the known resistances and estimated capacitances of the T_4 and T_5 circuits indicated that the T_4 circuit should have a smaller time constant than the T_5. Second, the analysis of the T_5 circuit assumed a perfectly sharp square wave; if the time constant of the rise of the square wave were greater than 0.05 μsec., then the above measurements would indicate that the time constant of the T_5 plate circuit was less than 0.05 μsec., which would be inconsistent with the known load resistance of T_5 and estimates of the minimum capacitance at the T_5 plate. Of course, this estimate of the time of rise of the square wave is for the case in which the square wave generator supplies calibrating pulses to the T_5 circuit. When the generator is connected to the experimental tube, the capacitance added and the flow of thermionic current in the experimental tube reduce the time constant of the rise of the square wave to about 0.2 μsec. From this analysis we conclude that thermionic current pulses of 0.1 μsec. time constant can be detected with this circuit, and pulses of time constant greater than about 3 μsec. can be accurately measured.

In using this circuit to measure the current *vs.* time characteristics of experimental tubes, we must assume that the thermionic current rises to its maximum value immediately that anode voltage is applied to the experimental tube. That this assumption is justified, if "immediately" is interpreted as "in less than 0.2 μsec.," can be inferred from the following experiment: Suppose that instead of using resistors R_{18} and R_{19} (Fig. 1) to generate a square wave for a calibrating pulse as outlined above, the experimental tube is connected to the resistance-capacitance pulsing circuit (R_{20} and one of the condensers C_{12} to R_{19}) by throwing switch S_4 into the lower position. This will be as effective in producing pulses of time constant 2 to 10 μsec. as the R_{18}, R_{19} circuit, provided the thermionic current rises to its maximum value in a time short compared to 0.2 μsec. This experiment was performed, and the result indicated that the thermionic current increased to its maximum value in less than 0.2 μsec.

Temperatures of the experimental tube cathodes were observed with an optical pyrometer. The brightness temperature of the actual emitting surface, rather than of the nickel core, was observed in order to avoid errors caused by temperature gradients in the coatings and to afford observation of any change in temperature with changes in thermionic current density. The spectral emissivity e_λ for optical pyrometry ($\lambda=0.65\mu$) of barium and strontium oxides is a matter of some disagreement; e_λ apparently varies with thickness of oxide layer,[1] state of aggregation of the oxide particles, and choice of core metal.[2] In the present work, e_λ was assumed to be 0.45 for all coatings; absorption in the glass envelope of the tube reduced the effective e_λ to about 0.40.

It is well known[3] that the temperature-limited current from an oxide-coated cathode is subject to wide variations. Two cathodes installed in different tubes, but constructed as nearly as possible identically, frequently yield widely different work functions. The emission from a single

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[1] P. Clausing and J. B. Ludwig, Physica **13**, 193 (1933).

[2] G. E. Moore and H. W. Allison, J. App. Phys. **12**, 431 (1941).

[3] J. P. Blewett, J. App. Phys. **10**, 688 and 831 (1939).

cathode will frequently change with time in an unpredictable manner. The temperature-limited emission depends markedly on the treatment of the cathode for the time just preceeding measurement. Glowing at a different temperature, drawing current at the same or different temperatures, application of strong fields, or allowing the cathode to operate space-charge limited—all affect the saturation current by unpredictable amounts. In addition, there are several time effects of a few minutes or a few seconds duration: Joule heating, poisoning of cathode by gas liberated from the anode, and a decay effect investigated by Blewett.[4]

It was only natural, then, that the attempts to measure short-time currents at first yielded data which were thoroughly scattered and quite unreproducible. The usual vagaries of oxide emitters here caused more than the usual error in measuring thermionic constants, since ten or fifteen minutes were required to obtain the decay characteristic at a single temperature (as contrasted with the few seconds required to read an ammeter if only steady current were being measured).

After considerable experimenting, the following technique of measurement was developed: (1) The cathode was glowed at $T+100°$ for about 55 sec. (glowing at $T°$ yielded the same results, but 5 to 10 min. were required instead of 55 sec.); (2) heater power was then reduced to an amount sufficient to maintain the temperature $T°$, and hence the cathode cooled to this temperature (one min. was allowed for cooling); (3) the square wave pulses were applied and measurement begun, the actual balance of the circuit being obtained 3 sec. after pulsing began. A reliable reading could not be taken in less than 3 sec., and measurement showed that the decay in this time was always less than 3 percent (3 sec. of pulsing entails less than 0.1 sec. of actually drawing current). This procedure was followed for each point on the current *vs.* time characteristic. At the end of a series of readings at a single temperature, an attempt was made to repeat the first of the series; if this could not be done within 2 or 3 percent, the entire series was discarded. A similar check was employed at the end of a group of characteristics for different temperatures. After six or eight characteristics were taken (in order to find the temperature dependence of the short-time decay effect), an attempt would be made to repeat several points on the first characteristic. If this could not be accomplished within 8 or 10 percent, all the characteristics were discarded and the cathode was aged by applying pulses to it for an hour before subsequent measurements. This procedure resulted in data much more reproducible and regular than are usually associated with oxide-coated cathodes.

When anode voltage was suddenly applied to the experimental tube, the charging of the anode-cathode capacitance necessitated a flow of displacement current through the resistance selected by S_3 (Fig. 1). This current was of the same order of magnitude as the smallest thermionic currents measured. By observing the displacement current with the cathode at room temperature and analyzing the circuit (including distributed capacitance) adjacent to the experimental tube, this displacement current could be determined and subtracted from the total observed current, yielding true thermionic cathode current.

It is not necessary to make a similar correction for the current resulting from abruptly collecting electrons from the "space-charge cloud" surrounding the cathode, since calculations based on the theory of Langmuir[5] show that this current is several orders of magnitude lower than the thermionic currents observed.

Current and time measurements with this apparatus were accurate to ±4 percent at any values of current and time considered, and to ±2 percent for all times greater than 10 μsec. Lack of knowledge of the spectral emissivity of oxide cathodes limited the accuracy of measurement of temperature to about ±2 percent.

III. A THEORY OF THE THERMIONIC CURRENT DECAY

Before discussing experimental results, we shall digress to propose a theory of the decay of thermionic emission during the short time interval (about a millisecond) after drawing of current is initiated. This theory is based on the assumption that the enhanced emission of oxide cathodes is

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[4] J. P. Blewett, Phys. Rev. **55**, 713 (1939).

[5] I. Langmuir, Phys. Rev. **21**, 419 (1923).

caused by a layer of barium atoms on the emitting surface. (We shall write "barium" for "barium, strontium, or calcium" except when referring to the work of other investigators.)

Langmuir[6] demonstrated that the electron emission from a metallic surface could be increased a million-fold if a layer of thorium atoms were adsorbed on the surface. This increase comes about because each "adatom" exists during a fraction (of the order of 0.1) of the time as a positive ion, having lost an electron to the metallic surface; Gurney[7] has showed that the average charge of an adatom depends on its distance from the metal. Becker[8] investigated films of barium on tungsten and on barium oxide.[9] His work with barium oxide confirmed the hypothesis proposed by Koller[10] and Rothe[11] that the enhanced emission from oxide-coated cathodes was caused by a surface layer of barium. The small A factor in the thermionic emission equation and the activation effects observed (Blewett[3]) with these coatings substantiated this hypothesis.

Becker[9] showed that unless barium was deposited on the cathode from an external source, the barium layer residing on the cathode surface was always thinner than that required for maximum emission. Thus any process which removes barium from the emitting surface should increase the thermionic work function. Such a process is evidently the drawing of thermionic current, since the electric field at the cathode surface necessary to sustain current flow forces barium ions away from the surface and into the interior of the cathode coating. The net flow of barium ions inward would cease when the rate of diffusion outward and subsequent ionizing of barium atoms equals the rate of removal of ions under the influence of the electric field. The electrolytic current density of barium ions is proportional to the electric field which is in turn proportional to the thermionic current density i. The diffusion current density is proportional to the concentration gradient of barium atoms, which is in turn proportional to the net number of atoms which have left unit area of the surface. Hence we obtain:

$$\frac{dN}{dt} = -\frac{\alpha i}{e} + \beta(N_0 - N), \tag{4}$$

where N is the number of adsorbed atoms per cm^2 of surface at the time t, i is the thermionic current density (amp/cm^2), e is the absolute magnitude of the electronic charge (coulombs), α is a constant proportional to the ionic mobility, and β is a constant proportional to the atomic diffusion coefficient and inversely proportional to the thickness of the layer in which the concentration gradient is set up. The subscript 0 refers here and hereafter to conditions at the instant drawing of thermionic current is begun, that is, at $t=0$.

Langmuir's[6] equation for the thermionic current from an emitter possessing a layer of adatoms is:

$$\log(i/i_{N=0}) = \theta \log(i_{N_c}/i_{N=0}), \tag{5}$$

where i_{N_c} is the current when $N=N_c$, $i_{N=0}$ is the current when $N=0$, $\theta = N/N_c$, and N_c is the number of barium atoms per cm^2 in a complete monatomic layer. From Becker's[9] data for barium films on tungsten or barium oxide we learn that Eq. (5) is not strictly correct. We can say, however, that

$$\log(i/i_{N_c}) = \theta L, \tag{6}$$

where L is a slowly varying function of θ; over the range of θ's producing a range of a factor of 10 in thermionic current, L is approximately constant. For θ near 0, $L \cong 2 \log(i_{N_c}/i_{N=0})$; for $\theta \cong 0.7$, $L \cong 0.6 \log(i_{N_c}/i_{N=0})$.

If we write an equation like Eq. (6), but with i_0 and θ_0 in place of i and θ, and subtract it from (6), we obtain:

$$\log(i/i_0) = L(\theta - \theta_0). \tag{7}$$

Differentiating (7) with respect to time and combining with (4) yields:

$$\frac{1}{i}\frac{di}{dt} = L\frac{d\theta}{dt} = \frac{L}{N_c}\frac{dN}{dt} = -L\beta(\theta-\theta_0) - \left(\frac{\alpha L}{eN_c}\right)i. \tag{8}$$

We can eliminate θ by using (7) again and obtain:

$$\frac{1}{i}\frac{di}{dt} = \beta \log\left(\frac{i_0}{i}\right) - \left(\frac{\alpha L}{eN_c}\right)i. \tag{9}$$

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[6] I. Langmuir, Phys. Rev. **22**, 357 (1923).

[7] R. W. Gurney, Phys. Rev. **47**, 479 (1935).

[8] J. A. Becker, Trans. Am. Electrochem. Soc. **55**, 153 (1929).

[9] J. A. Becker, Phys. Rev. **34**, 1323 (1929).

[10] L. R. Koller, Phys. Rev. **25**, 671 (1925).

[11] H. Rothe, Zeits. f. Physik **36**, 737 (1926).

Equation (9) represents approximately the dependence of thermionic current upon time.

Physical processes other than the one postulated might lead to Eq. (9). For instance, the density of barium adatoms might remain constant with time, but the average charge of each might decrease as current was drawn. If an adatom moves inward under the influence of an electric field, its average charge must eventually decrease, since it becomes indistinguishable from an interstitial barium atom and conductivity data[12] show that only a very small fraction of such atoms are ionized at 1200°K. Thus, the decay of the emitting power would be caused by a slight displacement toward the oxide, and consequent decrease in average charge, of the barium layer. However, it is probable that this process produces a steady state in a time of the order of 1 μsec., which is much shorter than the decay times observed in this investigation.

Let us define i_1 by:

$$\beta=\left(\frac{\alpha L i_1}{eN_c}\right)\left(\frac{1}{\log\,(i_0/i_1)}\right), \tag{10}$$

and write

$$\eta=i/i_1;\quad \eta_0=i_0/i_1;\quad \xi=(i_1\alpha L/eN_c)t. \tag{11}$$

We have as yet ascribed no meaning to i_1. Using (10) and (11), we find Eq. (9) becomes:

$$\frac{1}{\eta}\frac{d\eta}{d\xi}=\left(1-\frac{\log\eta}{\log\eta_0}\right)-\eta. \tag{12}$$

Consider the behavior of (12) as ξ increases from 0. When $\xi=0$, $t=0$, $\eta=\eta_0$. Initially, $(1-\log\eta/\log\eta_0)=0$, so the initial slope is $(d\eta/d\xi)=-\eta^2$; thus η decreases rapidly at first as ξ increases. The term $(1-\log\eta/\log\eta_0)$ slowly increases as η decreases. The asymptotic behavior of (12) for large ξ can be seen by separating the variables and integrating:

$$\xi=\int_{\eta_0}^{\eta}\frac{d\eta'}{\eta'(1-\log\eta'/\log\eta_0-\eta')}. \tag{13}$$

Evidently as the upper limit of the integral approaches 1, the integrand becomes approximately proportional to $d\eta'/(1-\eta')$; hence as $\eta\rightarrow 1$, $\xi\rightarrow\infty$. We thus identify the case $\eta=1$, $i=i_1$, with the steady state condition ($t=\infty$).

Returning to (12) we note that, although the variables are separable, this equation cannot be integrated easily as it stands. Furthermore, one cannot perform a single numerical integration and solve the problem completely, because of the presence of the parameter η_0. To obtain an approximation to $\eta(\xi)$ we shall write

$$1-\log\eta/\log\eta_0\cong 1/\eta. \tag{14}$$

This is not so severe an approximation as it may seem. The term represented by Eq. (14) is small relative to η except in the region near $\eta=1$; at $\eta=1$, Eq. (14) is exact. After obtaining $\eta(\xi)$ upon the basis of the approximation contained in (14) we shall compare our result with a numerical integration of (12).

Using Eq. (14), we find Eq. (12) becomes

$$d\eta/(\eta^2-1)=-d\xi. \tag{15}$$

Upon integrating, we obtain

$$\xi=\tfrac{1}{2}\log\left[\frac{(\eta+1)(\eta_0-1)}{(\eta-1)(\eta_0+1)}\right], \tag{16}$$

or, solving (16) for η,

$$\eta=1+\frac{2}{\left(\dfrac{\eta_0+1}{\eta_0-1}\right)\epsilon^{2\xi}-1}. \tag{17}$$

Figure 5 shows $\eta(\xi)$ from Eq. (17) for three different values of η_0. The dots in Fig. 5 are the results of a numerical integration of Eq. (12) for the case $\eta_0=11$. Evidently $\eta(\xi)$ as given by (16) provides a solution of Eq. (12) that is sufficiently accurate for the purpose of comparison with the experimental data presented below.

IV. EXPERIMENTAL RESULTS

In this section we shall report successively five features of the experimental results, and compare each with predictions based on the hypothesis proposed above. We shall use results from five tubes for each of these features, and in connection with the dependence of the decay on coating thickness we shall use the results of two additional tubes (No. 3 and No. 4, to which the

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[12] W. Meyer and A. Schmidt, Zeits. f. tech. Physik **13**, 137 (1932).

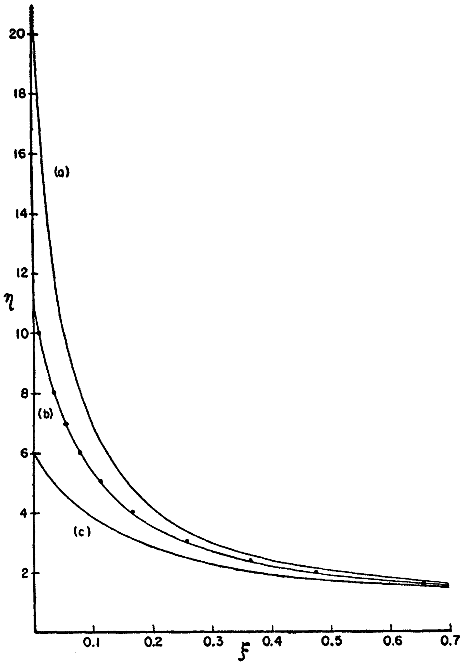

FIG. 5. $\eta(\xi)$ for three values of η_0.

measurement cycle of glowing and pulsing described in the first section was not applied).

All of the data exhibited in Figs. 6–8 and in Table III were taken under the following conditions: (1) Anode voltage was applied to the tubes in pulses of about 300-μsec. duration; (2) these pulses were repeated at the rate of 30 per sec.; (3) between pulses, a small retarding field was applied to the cathode; (4) the amplitude of the anode voltage pulse was 450 volts.

1. Current as a Function of Time

Figure 6 shows the decay of thermionic current at a fixed cathode temperature. The solid line is a plot of Eq. (16) with the scale factors (ξ/t) and (η/i) and the parameter $\eta_0(=i_0/i_1)$ chosen to give the optimum fit; the dashed line is a fit of the exponential function, $i=A+B\exp(-t/\tau)$, to the same data. Equation (16) evidently represents the experimental data much more closely than does the simple exponential function.

Figure 7 shows decay characteristics of tube No. 11 at 3 different cathode temperatures. The scales for the 3 temperatures are different, and the solid lines were obtained from Eq. (17). Equation (17), with the three adjustable constants properly chosen, represents the data of Fig. 7, and all of the 25 decay characteristics obtained, with error of about the same magnitude as the scattering of the experimental points.

By fitting Eq. (17) to data on 5 tubes, the values of i_0 (initial current) and i_1 (final current) portrayed in Fig. 8 were obtained; all the points above the dashed line represent i_0, all those below are values of i_1.

2. Dependence of Decay on Cathode Thickness

Table I shows the compositions and thicknesses of the cathode coatings studied. Since the points in Fig. 8 from tubes No. 8 and No. 11 practically coincide, we conclude that the "range" i_0/i_1 of the decay phenomenon does not depend on cathode coating thickness, at least when this thickness is of the order of a few mg/cm.[2] Furthermore, tubes No. 3 and No. 4 produced nearly identical results for range and rate of decay. Comparison of Table I and Fig. 8 indicates that the two different compositions of coating material produced about the same decay range.

Tube No. 14 exhibited less range of decay than the others. The cathode of this tube was removed and examined. About one-half of the cathode area looked as if most of the oxides had been removed during activation and use, leaving a layer of oxide more or less combined with the nickel core. The tube No. 12 currents show a more marked dependence on temperature than exhibited by other tubes, which suggests that the cathode in this tube may have been incompletely activated.

Consequently, these data indicate that over a wide range of thickness of oxide coatings the initial and final currents at a particular tempera-

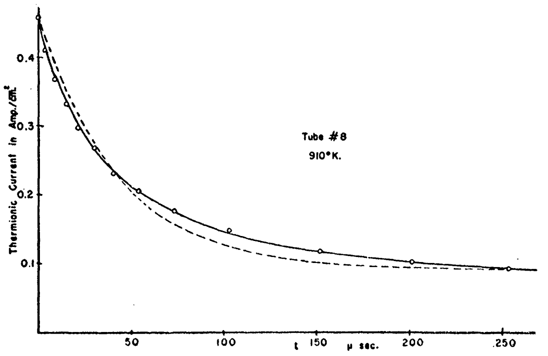

FIG. 6. Decay characteristics.

ture are substantially constant. On the other hand, Eqs. (4) and (10) require that the final current be inversely proportional to the thickness of the layer in which the electrolytic conduction and diffusion take place. Thus this layer cannot be identified with the thickness of the cathode coating, but must be a layer of the same thickness in all coatings. Such a layer could arise because of the granular nature of the oxide cathode. Within any single oxide particle, electrolytic conduction may be a substantial fraction of the total current. The conduction between two adjacent oxide particles should be largely electronic, since the wave-length of a barium ion is much greater than that of an electron, and hence an electron can more easily cross the gap between particles. The diffusion-conduction layer would thus be the layer of oxide particles lying at the emitting surface. In the cathodes used in this investigation, this layer would be about 2 microns in thickness.

According to this barium conduction hypothesis, the steady-state current i_1 should increase as the size of oxide particles decreases. This is because there is no reason to believe that i_0 should depend sensitively on particle size, but the logarithm of the decay ratio i_0/i_1 should be proportional to the thickness of the particles composing the cathode surface. Benjamin, Huck, and Jenkins[13] investigated the dependence of thermionic current upon size of oxide particles and found an increase in steady-state current with decreasing particle size.

Measurement of the ratio of thermionic current decay i_0/i_1 on a cathode composed of a single, fairly thick crystal of barium oxide should indicate whether or not this electrolytic conduction hypothesis can be correct. If it is correct, the thermionic emission from such crystals should be extremely small when current is drawn continuously.

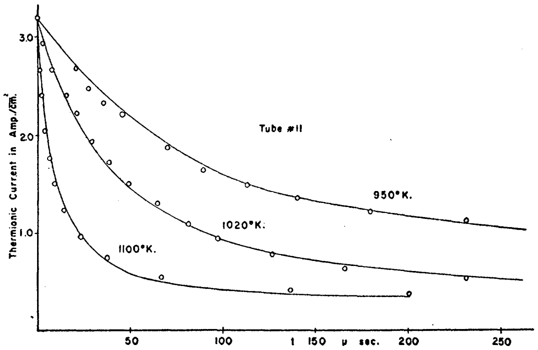

FIG. 7. Decay characteristics.

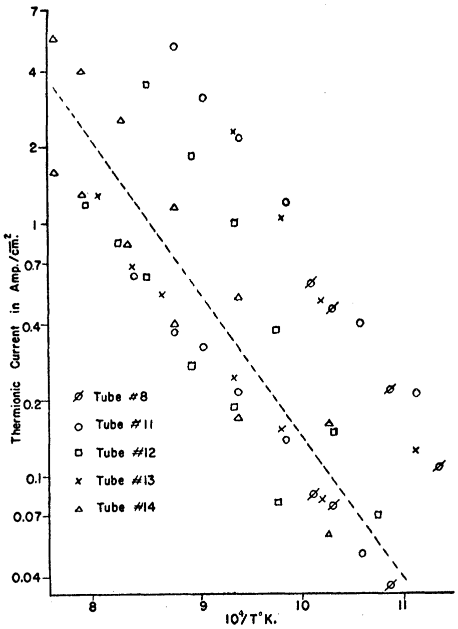

FIG. 8. Initial and final currents.

If the emitting surface decays by electrolytic conduction, increasing the electronic conductivity of the cathode coating should decrease the ratio of decay. This suggests that in order to obtain larger values of i_1, which for most purposes is the only useful current, we might try to maintain layers of barium on materials with greater electronic conductivity than barium oxide but with the same or smaller work function. It might, for example, be possible to maintain barium films on silicon, which apparently meets the above requirements.

3. Anode Voltage Effect and Recovery Time

All the data reported so far were taken with an anode-cathode potential difference of 450 volts. This potential difference is about 3 times as large as necessary to prevent space-charge limitation of cathode current at the highest observed current densities. Such a potential produces, of course, an

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[13] M. Benjamin, R. J. Huck, and R. O. Jenkins, Proc. Phys. Soc. **50**, 345 (1938).

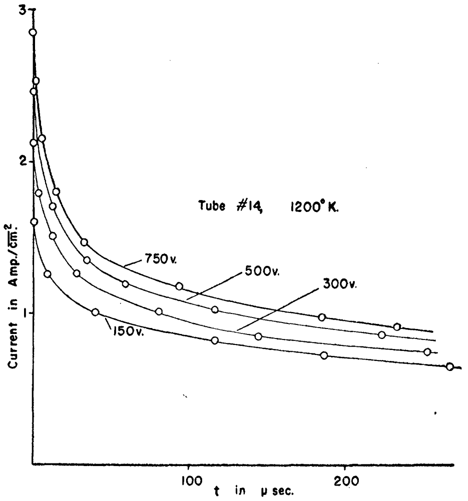

FIG. 9. Anode voltage effect.

appreciable Schottky effect in the thermionic emission.

The effect on the decay phenomenon of changing the electric field applied at the cathode was naturally of interest. Accordingly, the data plotted on Fig. 9 were taken; this plot shows decay characteristics of tube No. 14 at a cathode temperature of 1200°K, with four different values of anode potential differing in magnitude by a factor of 5.

Figure 10 shows plots of log i_0 *vs.* (anode voltage)$^{\frac{1}{2}}$ and log i_1 *vs.* (anode voltage)$^{\frac{1}{2}}$. The slope of the i_0 line in Fig. 10 corresponds to an anode voltage effect about $2\frac{1}{2}$ times the effect calculated from the tube geometry and the assumption that the emitter acted as a pure metallic surface. The slope of the i_1 line is about twice the value calculated on these assumptions. Such deviations are to be expected with oxide-coated cathodes or other composite surfaces, where some "patches" of the emitting surface have lower work functions than others.[14]

The difference in slopes between the i_0 and i_1 lines in Fig. 10 is easily explained on the basis of the theory we have proposed. Since the amount of surface positive charge which disappears when current is drawn is proportional to the emission current density, the patches which have the lowest work function will deteriorate most when current is drawn. The passage of current thus increases the work function of the patches of lowest work function more than it increases the work function of other patches. The variation of work function over the surface is therefore more extreme in the i_0 case, before appreciable current has been drawn, than in the i_1 case, and hence i_0 is a more sensitive function of anode voltage than is i_1.

Since all data assembled in Fig. 8 were taken at the same anode potential, these measurements have not been corrected for the anode voltage effect.

An investigation was also made to determine whether the decay depended sensitively on the duration of the current pulse or the rate at which pulses were repeated. At a fixed repetition frequency of 30 cycles per sec., changing the duration of drawing current (the width of the current pulse) from 100 to 300 μsec. produced no change in the decay ratio or decay rate. Similarly, at a fixed pulse width of 300 μsec., changing the repetition frequency from 20 to 120 cycles per sec. produced no change in the phenomenon. At 600 cycles, the ratio i_0/i_1 was decreased by about 20 percent from its value when relatively longer periods were allowed for the cathode to recover; this datum was taken on tube No. 8 at a cathode temperature of 920°K. This result is not very reliable, and the recovery time could not be further decreased, because of the design of the square wave generator and time measuring circuits. When the pulse width was an appreciable fraction of a cycle the power dissipating ability of some of the circuit elements was exceeded and certain potentials could not be kept fixed.

4. Work Functions

Using Fig. 8 we can compute values of ϕ' in the equation for thermionic emission from an elec-

TABLE I. Composition and thickness of cathode coatings.

Tube	Composition (by weight)	Thickness (mg/cm^2)
No. 3	60% BaO, 30% SrO, 10% CaO	0.7
No. 4	60% BaO, 30% SrO, 10% CaO	16
No. 13	60% BaO, 30% SrO, 10% CaO	32
No. 8	50% BaO, 50% SrO	1.2
No. 11	50% BaO, 50% SrO	5.2
No. 12	50% BaO, 50% SrO	9
No. 14	50% BaO, 50% SrO	0.8

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[14] A. Rose, Phys. Rev. 49, 838 (1936).

tronic semi-conductor:[15]

$$i = AT^{5/4}\exp(-\phi' e/kT), \tag{18}$$

or we can compute values of ϕ in the ordinary equation for thermionic emission from a pure metallic surface;

$$i = AT^{2}\exp(-\phi e/kT). \tag{19}$$

With the help of Fig. 10, we can correct the values of ϕ' and ϕ for the anode voltage effect. When this is done, we obtain the values shown in Table II, representing approximately the behavior of tubes No. 8, No. 11, and No. 13.

These results appear anomalous in that the steady-state current i_1, though smaller than i_0, corresponds to a lower work function than the initial current i_0. However, we must not regard these values of ϕ' as literally work functions. Equation (18) is valid only if the surface potential barrier is absolutely fixed in magnitude, independent of temperature. A small change with T of the barrier height would, of course, make a significant change in the measured value of ϕ'. If, as we supposed in the last section, the copious thermionic emission arises from the existence of a surface layer of barium, the fraction of the surface covered with active metal can easily change with T. According to Becker,[9] a change in θ from 0.2 to 0.3 produces a change of at least a factor of 10 in the thermionic emission. Thus only a small change with temperature of θ_0 or θ_1 or both would be required to produce this divergence of the i_0 and i_1 lines.

5. Rate of Decay

Our experimental data yield values of $t/\xi = eN_c/i_1\alpha L$, which measures the time of decay. Before we can obtain values of α from these results we must know L and N_c.

From the information presented in conjunction with Eq. (6), we see that L decreases from about 2 log $(i_{N_c}/i_{N=0})$ to about 0.6 log $(i_{N_c}/i_{N=0})$ as θ, the fraction of the surface covered with barium atoms, increases from 0 to 0.7. To get an estimate of log $(i_{N_c}/i_{N=0})$, we use the measurement by Becker.[9] He observed currents differing by a factor of 10^5 as barium atoms were brought to the emitting surface electrolytically by sending a stream of electrons into an oxide coating from the vacuum. He believed that his surface may have had some barium adsorbed on it at the beginning of the experiment, so the actual ratio $i_{N_c}/i_{N=0}$ may have been 10^6 or 10^7. Of course, his cathode coating may have differed considerably from ours, but we shall probably not err greatly if we assume log $(i_{N_c}/i_{N=0}) \cong 15$. Then L should decrease from about 30 for dilute films to about 10 for $\theta \cong 0.7$.

TABLE II. Work functions.

	ϕ'	ϕ
i_0	1.17 v	1.12 v
i_1	0.98 v	0.91 v

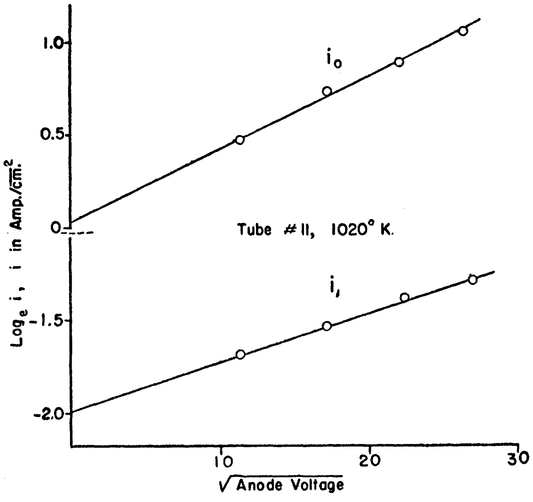

FIG. 10. Schottky lines.

The value of N_c is also subject to a certain amount of doubt. Both BaO and SrO form face-centered cubic crystal lattices, with the fundamental cubes about 2.77A and 2.58A, respectively, along an edge. If the (100) plane of the lattice lies in the surface, there should be about 2.8×10^{15} atoms per cm^2 lying at the surface, for either BaO or SrO. Metallic strontium forms a face-centered cubic lattice, 6.06A on a side. If we assume that the distance of closest approach of strontium atoms in a surface layer is the same as the distance of closest approach in solid strontium, there should be about 6.3×10^{14} atoms per cm^2 on the surface. Barium has an edge length of the fundamental cube equal to 5.01A, but it is a

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[15] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, London, 1936), second edition, p. 401.

TABLE III. Values of αL.

Temp., °K	Tube No. 8	Tube No. 11	Tube No. 12	Tube No. 13
920	5.1			
950		3.9		
970	5.2			
980				3.9
990	5.4			
1020		2.1	1.6	3.7
1070		3.1	1.7	5.0
1100		3.1		
1120			1.3	
1150		3.2		
1180			1.3	

body-centered cubic lattice, and hence yields about the same density of surface layer as strontium. Thus, we might expect in a complete monolayer about one adsorbed atom to every 4 atoms of the crystal surface. We shall assume that N_c equals 6×10^{14} atoms per cm^2.

Table III shows the values of αL computed from the decay characteristics of 4 tubes at several different temperatures. In this table are fifteen determinations of this quantity, corresponding to the fifteen point pairs (i_1 and i_0 at a particular temperature) in Fig. 8. (Actually, Fig. 8 contains 53 points, but 11 of these are values of i_0 for temperatures at which i_1 could not be measured, or vice versa; another 12 points represent data from tube No. 14, which are not included here because of the considerations presented in the preceding section.) It appears that αL is sensibly constant for any one tube over a wide range of temperatures and currents.

It will be recalled that $\alpha i/e$ is the net number of ions leaving the surface per sec. per cm^2 when the current i flows. If the entire current in the region near the surface were borne by singly-charged barium ions, then $\alpha=1$. If only part of the current in this region were electrolytic, α might equal any number less than 1.

The data in Table III, with the interpretation of these data based on Eq. (4), indicate that a large fraction of the current in a single small crystal of BaO is carried by barium ions. Using the limits we have placed on L and values from this table, we see that this fraction is at least 5 percent and at most 50 percent. Measurements of the electrolytic conductivity of BaO have been made by Becker;[9] he estimated that about 1/200 of the current in BaO at 800°K is carried by barium ions, and a smaller fraction at higher temperatures. But his measurements were of the conductivity of cathode coatings, rather than of single crystals of BaO. By the argument put forward in connection with the dependence of the decay on thickness, we should expect that the fraction of conduction current borne by barium atoms should be much greater for a single crystal than for an aggregation of small crystals. Thus, Becker's measurements are not in conflict with the interpretation placed on values in Table III, provided that the distinction between the conductivity of a cathode coating and of a single BaO crystal is valid. We must use the fact that the conductivity of small BaO crystals packed together is largely electronic to explain the lack of dependence of the ratio i_0/i_1 on the thickness of the cathode coating.

This short-time decay effect is quite possibly related to the "flicker effect" originally observed by Johnson[16] and discussed by Schottky.[17] The latter effect is the great increase in shot noise in diodes with oxide-coated cathodes when the frequency of the pass-band of the amplifier with which the noise is measured is decreased below about 5000 cycles per sec. Schottky estimated that a surface process of some kind (re-orientation of surface atoms or change in work function of the surface at a localized spot) which has a characteristic time of the order of 10^{-3} sec. must be postulated in order to account for Johnson's data. Unfortunately, the temperature at which these data were taken was not reported, but if this temperature were about 900°–1000°K, the decay we have investigated would occur in about the proper time interval to be the process Schottky requires.

Part of the work presented in this paper was carried out while the writer held a Charles A. Coffin Fellowship. The author is particularly indebted to Professor Lloyd P. Smith for suggesting this study and for frequent suggestions and assistance in the course of the work.

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[16] J. B. Johnson, Phys. Rev. **26**, 71 (1925).

[17] W. Schottky, Phys. Rev. **28**, 74 (1926).