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# Electrical and Luminescent Properties of Willemite Under Electron Bombardment

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An insulated surface uniformly bombarded with electrons of a given energy attains a potential relative to other elements in a high vacuum tube such that exactly as many electrons leave the surface by secondary emission as there are primary electrons arriving. A tube and circuit have been constructed for determining accurately this potential for willemite surfaces while being bombarded by electrons of energy range up to 10,000 volts. It was found that the surface potential was only slightly negative with respect to the most positive anode of the tube over the lower range of energy but finally reached an upper limit of potential relative to the cathode usually between 6000 and 7000 volts. The resistance between wires covered by the willemite was found to be independent of the bombarding current and voltage except in so far as this bombardment changed the temperature of the material. A special potassium phototube is described which was used to determine the light output from the bombarded surface as a function of the current density and the electron energy. The light was found to be accurately proportional to the current for densities below  $2.5 \times 10^{-6}$  amp. per sq. cm but above this a saturation effect set in quite gradually so that with a current of  $20 \times 10^{-6}$  amp. per sq. cm the light output was

### INTRODUCTION

M ATERIALS which luminesce under electron bombardment have been used in "electron projection" tubes by Johnson and Shockley<sup>1</sup> and others to study the electron emission from hot filaments by accelerating the electrons from the filament to a coaxial glass cylinder coated internally with a luminescent substance. In order to make these thermionic studies more quantitative, we needed to know more about the electrical and luminescent properties of the phosphors used and therefore undertook what was originally intended to be a brief investigation along this line. The results obtained

<sup>1</sup> R. P. Johnson and W. Shockley, Phys. Rev. **49**, 436 (1936).

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only 65 percent of the value which it would have been had the light intensity per unit current density remained constant. The light output for a constant current was found to increase with  $(V - V_0)^2$  where  $V_0$  is the "dead voltage" when the bombarding energy was less than that required to penetrate through the individual grains of the willemite. An experimental nine-inch cathode-ray tube was also studied for screen potential and light output as a function of current density and anode voltage. The difference in potential between the screen and the anode was again small for the lower range in voltage but with anode voltages above 7000 volts, the apparent screen potential depended on the current density so that a change of potential of the screen of as much as 1500 volts was observed as the current density was increased from one to ten milliamperes per sq. cm. The light output increased with the square of the bombarding potential up to 1500 volts but above this it increased with the 1.2 power of the voltage. The light output per unit current density observed at 10-2 amp. per sq. cm was only two percent of that observed at  $10^{-6}$  amp, per sq. cm on account of the severe "saturation" effect found at high current densities.

seem to be of sufficient general interest to warrant their publication in spite of the fact that the tube design would have to be improved before one could maintain that the results were entirely free from possible adverse criticism. Since it would require a longer time to make the necessary improvements than there will be available to the writer in the near future, it has been thought best to bring forward the results which are available to date with the hope that the work will be extended and made more quantitative in this laboratory or some other.

#### **OBJECTIVES**

It is obvious that the potential of a phosphor, when under electron bombardment, will adjust itself relative to the other elements of the tube so that there will be no accumulation of charge. If the phosphor is entirely insulated, either secondary electron emission or the arrival of positive ions or both of these processes must be invoked to keep the potential constant. In "sealed-off" tubes the effect of the ions can be made entirely negligible. The first objective therefore was the investigation of secondary emission properties of certain phosphors. Since in most practical applications it is possible to make contact with the phosphor either by supporting it on conducting material or by making contact at the edge, the second objective was to determine the resistivity of phosphors under operating conditions.

With the potential of the luminescent material known, it is clear that the third and fourth objectives of this study would naturally be the determination of the light output as a function of the true bombarding potential of the phosphor relative to the cathode and as a function of the current density.

# TUBE AND CIRCUIT DESIGN

The sketch shown in Fig. 1 shows the essential parts of the tube used. This drawing has been prepared to illustrate certain features of construction rather than attempt to draw an exact reproduction of the tube. Seven single lead tungsten-to-glass seals were arranged around the end of a large Pyrex "test-tube" with a bottom view lay-out as shown in Fig. 1b. A side tube with a short tungsten seal for mounting the "getter ring" was sealed as shown in Fig. 1a, and the blank thus prepared was connected to an exceptionally good vacuum system for the preliminary baking of three or four hours at 500°C. This served to anneal the glass partially and give the seals a rigorous test since the oven was allowed to cool very slowly after this bake. The blank was then cracked open by using a hot wire at the point marked "crack-off" and the metal parts which had all been vigorously heat treated in a separate blank were assembled as shown. The parts were carefully aligned so as to be concentric and the slits 1 and 2 properly located.

Two "fernico" wires 20 mils in diameter and 10 cm long were imbedded in small tubes of 705-AO glass. At one end, these were in turn

melted into a small plate of this glass which was finally ground to form a flat rectangular plate 0.55 cm by 0.95 cm with short sections of the "fernico" exposed as shown in Fig. 1c. The phosphor was applied to this surface by one of the following three methods. (1) An air operated spray gun was used for the moderately fine grain phosphors which were suspended in acetone. The grains were sufficiently course so that constant agitation by air bubbling was needed to keep the phosphor in suspension. The spray was operated in this way until the coating was thick enough to hide completely the "fernico" wires lying in the surface of the test plate. (2) The very fine grain phosphors were furnished to me in the form of a "milk-like" suspension in acetone. In this case the grains were so fine that some hours were required for the phosphor to settle out after the suspension had been agitated. The grain size was estimated to average approximately  $3 \times 10^{-5}$  cm



FIG. 1. (a) Sketch of tube. (b) Bottom layout of tube blank. (c) Test plate with "fernico" wires exposed in surface.

in diameter. It was found quite practical to place a single drop of this suspension on the test plate and allow the acetone to evaporate thus leaving a uniform and well adhering coating of the phosphor. (3) Still a third method used for very coarse grains utilized a water solution of potassium silicate for a binder.

After the test sample was prepared, movable glass sleeves were slid over the two glass-covered wires which formed the support of the test sample. These wires were welded to the tungsten leads marked  $P_1$  and  $P_2$  in Fig. 1 in such a manner that the test plate fitted into the 0.6 cm by 1.0 cm opening in the second anode shown as  $A_2$ . After the welding was completed the glass sleeves were adjusted to cover the welds completely. These sleeves were formed so as to fit very closely over the glass-covered "fernico" wires and also over the glass of the tungsten-to-glass seal. It was very important that no part of the test plate leads be exposed to the direct arrival of electrons since the method used to study the electrical properties of the phosphor depended on the assumption that no charges could flow into the test plate connections except those which flowed through the phosphor.

A thoriated tungsten filament which had been polished smooth by grinding was used as the source of electrons because experience has shown that this type of filament emits electrons very uniformly after prolonged activation at about 1960°K subsequent to giving the filament the usual high temperature flashing at 2850°K. It was also possible, with this type of cathode, to open the tube as many times as desired to change the phosphor sample and at the same time not impair in any way the emission properties of the filament. Of course the filament had to be reactivated but this could be done with the same degree of perfection as often as was needed.

The four cylinders used for the first anode  $A_1$ , the second anode  $A_2$  and the guard rings  $G_1$  and  $G_2$  were made from annealed 3 mil sheet tantalum and supported on tantalum wires so that these parts could be heated nearly to a "white-heat" by electron bombardment and induction heating. Short pieces of outgassed nickel were used to assemble these metal parts to the tungsten leadin wires. Eight to ten aluminum-barium getter pellets<sup>2</sup> were welded in the form of a ring and mounted in the side-tube shown in Fig. 1. This construction was used because of the ease with which this unit could be cracked off to be cleaned and replenished with getter each time a new phosphor sample was put in the tube.

After the tube was completely assembled and sealed back together at the "crack-off," the exhaust schedule lasting between ten and thirty hours was started. After a one-hour bake at 500°C and about three hours at 470°C, during which time the liquid-air trap and the connection between it and the tube were also baked at the same temperature, liquid air was put on the trap and following this the "tube oven" and the "connection oven" were removed. The filament was then flashed and activated and the bombardment of the anodes begun. This was continued until a vacuum of the order of 10<sup>-8</sup> mm of mercury was obtained with the first anode nearly at a "white-heat" and the getter ring at as bright a red as was considered the maximum which would not explode the getter. During the early stages of heat treatment it was found that the gas given off, rapidly deactivated the filament as indicated by a considerable decrease in electron emission. The time required to bring about this deactivation served as a better indication as to the condition of the tube than any measurements which could have been made with an ionization gauge. The tube was operated at about ten times the normal maximum load during this heat treatment in that ten to fifteen milliamperes of electron current flowed from the filament to the anodes with a difference in potential between the filament and these collecters of 10,000 volts. Most of the heat thus developed was radiated by the first anode and therefore the outer electrodes  $A_2$ ,  $G_1$  and  $G_2$  were heated red hot by high frequency induction currents. The heat treatment of these outer elements was limited because it was feared that the glass test plate might melt. When it was found that under these conditions the filament remained well activated for a period of an hour or so, the seal-off capillary was softened and the getter ring heated to explode the

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<sup>&</sup>lt;sup>2</sup> Type C-400 barium-aluminum getters very kindly furnished by King Laboratories, Syracuse, N. Y., were found to be particularly satisfactory since they will withstand baking at 500°C for long periods of time without appreciable evaporation before firing.

getter. The tube was finally sealed off after another hour or so of heat treatment and pumping. After this rather vigorous exhaust schedule, the tube could be operated indefinitely at 10,000 volts with as much as one milliampere of current to the anodes without appreciable loss of activity of the cathode surface.

The diagram of the electrical circuit used for this study is shown in Fig. 2. Three power-packs using full-wave rectifiers and adequate filtering were connected as shown. Pack  $(Pa_2)$  maintained the required voltage difference between the second anode and the filament while pack  $(Pa_1)$ was used to maintain the first anode at any potential, relative to the second anode, that was needed. These power-packs and also the filament batteries were well insulated from ground. A third pack  $(Pa_g)$  was used to establish the second anode at any desired potential relative to ground. The test wires connected to the phosphor were always at ground potential as can be seen from the circuit diagram.

# MEASUREMENT OF POTENTIAL AND RESISTANCE OF PHOSPHOR WHILE BOMBARDED BY ELECTRONS

The potential difference between the second anode and the cathode will be designated as  $V_{ac}$ while that between the second anode and the first anode will be given by  $V_{a1}$ . The symbol  $V_{ag}$ will be used to indicate the potential of the second anode relative to ground. The current to the anodes was controlled by varying the temperature of the filament. Although in general the current to the first anode was set at arbitrary values between  $10^{-8}$  amp. and  $3 \times 10^{-3}$  amp., the current measured at the second anode was assumed to be directly proportional to the primary beam current. That it was necessary to make this assumption, is obviously a serious criticism of this work. Many experimental results such as the accurate proportionality between light output and current for low intensities gave "internal" evidence that this assumption was justified but none of these gave incontrovertible information. If this problem is reattacked with the aim of making it more quantitative than the present study, the tube should be so constructed that the primary beam current can be measured

directly. The fraction of the primary beam which struck the phosphor on the test plate depended to a certain extent on the ratio of the potentials  $V_{a1}$  to  $V_{ac}$  since the slit in the first anode distorted





the equipotentials and thus created an electron lens which was converging or diverging depending upon the  $V_{a1}$  to  $V_{ac}$  ratio. Whenever measurements made at one value voltage  $V_{ac}$  were to be compared with those at another value of  $V_{ac}$ , the ratio  $V_{a1}/V_{ac}$  was maintained constant. With a filament diameter of  $5.06 \times 10^{-3}$  cm and first and second anode diameters of 1.0 and 3.81 cm, respectively, the ratio  $(V_{a1}/V_{ac}) = 0.20$  gave the critical condition for an electron lens of infinite focal length at the slit in the first anode. The lens formula given by Calbick and Davisson<sup>3</sup> predicted correctly the potential ratio required to focus an electron image of the filament on the phosphor surface. This formula is  $L=4(V_{ac}-V_{a1})/(G_2-G_1)$ , where L is the focal length in cm and  $G_1$  and  $G_2$  are electric intensities in volts per cm on the inside and the outside of the first anode computed disregarding the slit.

Secondary electrons produced at the slit of the first anode or even inside this anode could strike the phosphor test surface in case it was positive with respect to this anode. If the phosphor was less than one or two hundred volts positive with

<sup>&</sup>lt;sup>a</sup> C. J. Calbick and C. J. Davisson, Phys. Rev. **45**, 764 (1934).

respect to the first anode these secondaries tended to charge the surface to a more negative value relative to the second anode than it would have had in the absence of these low energy secondary electrons. On the other hand if the phosphor was between three hundred and a thousand volts positive with respect to the first anode then the secondary electrons arrived at the screen with enough energy to remove more than one electron for each of these electrons received at the screen. It will be shown below that as the energy of the primary electrons is increased a value is generally reached for which only one secondary electron is produced at the screen for each primary electron which strikes it. Unless some other agency is brought in, it is impossible to make the screen more positive with respect to the cathode than this limiting value. If only ten to twenty percent of the primary electron current is removed by conducting it away through the phosphor then a considerably higher cathode to screen voltage may be attained. Still another way of discharging the screen which might be worth consideration would be to bombard it with electrons from an electron "gun" entirely auxiliary to the principle electron gun of the tube. This auxiliary gun would spray the surface of the phosphor with a copious supply of three or four hundred volt electrons and since each one of these would produce more than one secondary electron at the screen, a considerably higher voltage difference could be maintained between the screen and the cathode of the principal gun of the tube.

With the circuit shown in Fig. 2, the potential



FIG. 3. Screen potential as a function of the first anode potential showing effect of secondary emission from first anode.  $V_{ac} = 2000$  volts.

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of the insulated phosphor could always be determined with accuracy since this was obtained by adjusting the voltage of the power pack  $(Pa_a)$ to that particular voltage for which no current flowed in the electrometer circuit. Since this part of the circuit was so sensitive that a current less than 0.001 percent of the primary beam current could be measured easily, it was possible to determine  $V_{ag}$  with high precision. A necessary condition that such determinations were not faulty was that the voltage  $V_{ag}$  for zero current should be independent of the beam current and be the same for either probe wire  $P_1$  or  $P_2$  or for both of them together. In the rare cases where these tests were not satisfied, definite faults in the screen were discernible. Although the screen potential could be determined with accuracy under any particular set of conditions, the results were not always entirely free from ambiguity because of the effects of secondary emission from the first anode. A particularly striking example of the effect of secondary emission is illustrated by Fig. 3. Here the observed value of  $V_{ag}$  for zero current through the probe connections is plotted as the ordinate and the difference in potential between the first and second anodes is plotted as the abscissa. The potential of the second anode relative to the filament was constant at 2000 volts and the phosphor used for this was a zinc silicate (meta) supported by a potassium silicate binder. The resistance of this phosphor was the lowest of any measured.

The curve shown in Fig. 3 started with  $V_{ag} = 320$  volts when the first and second anodes had no difference in potential. It is certain that a negligible number of secondaries from the first anode reached the screen under this condition and therefore we can conclude that for this particular phosphor and binder, an insulated screen would charge up to a potential of about 300 volts negative with respect to the anode when the true energy of the bombarding electrons was 1700 volts. This is an abnormally large difference in potential for such low energy electrons but this curve was selected for discussion to illustrate as clearly as possible the effect of secondaries which took place as the first anode was made nearly as negative as the phosphor. At first the phosphor became still more negative with respect to the anode as it received the very low energy secondaries which necessitated a drop in the primary beam energy from 1700 to 1600 volts in order to increase the normal secondary emission vield of the phosphor enough to make up for the arrival of the slow electrons. A discontinuity took place when  $V_{a1}$  was increased to 410 volts. The potential of the insulated screen changed suddenly over 200 volts and, with the first anode 570 volts negative to the second anode, the screen was only



FIG. 4. Potential difference between screen and second anode as a function of second anode potential. A, coarse grain phosphor with potassium silicate binder. B, very fine grain phosphor with no binder.

170 volts negative as compared with 320 volts which was the true value for the primary electrons taken alone. Under these conditions, the difference in potential between the first anode and the screen was 400 volts which further study showed to be the electron energy value giving the maximum secondary emission yield for this particular phosphor. In all of the work described below care was exercised in order to interpret the results correctly and not allow the effects of secondary emission from the first anode to invalidate the final conclusions.

The two curves shown in Fig. 4 illustrate the nature of the results obtained. These curves should be compared with that of Fig. 13 which was obtained with an experimental nine-inch cathode-ray tube with a very high current density  $(10^{-2} \text{ amp. per sq. cm})$  in the beam. The main points of interest in these curves are (1) at low voltages there is very little difference in potential between the screen and the second anode: (2) at higher voltages large differences come in and (3) a limit is reached as  $V_{ac}$  is increased such that the potential  $V_{ag}$  increases just as rapidly as  $V_{ac}$ . When this limit is reached it is impossible to obtain any increase in the bombarding electron energy by increasing the anode potential unless some other means of discharging the screen is used besides that of the simple production of secondary electrons by the primary beam. The two methods most commonly used are (1) screen conductivity and (2) the use of positive ions produced along the path of the primary beam. As was pointed out above, a third method perhaps worth trying would be to use an auxiliary electron gun.

It is obvious from the curves of Fig. 4 that zinc orthosilicate can have very different secondary emission properties depending on the method of handling it or on the type of binder used and the kind of impurities that may be present. Curve "A" was observed with a coarse grained phosphor held to the test plate by a potassium silicate binder and curve "B" was obtained with a very fine grained phosphor put on the test plate by the "drop" method described above. One phosphor studied which happened to have a maximum attainable potential of only 5600 volts in its normal state was found to change this maximum to about 8000 volts as a result of the evaporation of a small amount of thorium from the filament on to the surface of the phosphor. The thorium evaporated over probably formed on the average less than a monatomic layer. The increase in the voltage maximum thus obtained was not permanent and the experiment was useful only to indicate that very small amounts of impurity are needed to modify the secondary emission properties very considerably.

With the circuit arrangements as shown in Fig. 2, the resistance of the phosphor could be measured when it was not being electron bombarded by measuring the current flowing around the circuit as a function of the voltage difference applied between the probe wires. The current was found to be a linear function of the voltage up to

ten volts in either direction. Tests were not made with higher voltages. In order to measure the resistance of the phosphor while it was being bombarded, it was first necessary to set the voltage  $V_{aq}$  to that value for which no current flowed in the probe wire connected directly to the electrometer. This was done with the other probe connection open. After satisfying this condition an e.m.f. of about one volt was connected between the probe wires and the current flowing in the electrometer circuit due to this e.m.f. was measured. In all experiments of this kind which were tried there was no difference in the resistance due to the bombarding electrons except in cases where the heating effect was great. In most cases it was possible to reduce the resistance to one-half its original value by heating the phosphor with electron bombardment. The fact that this was a heating effect was shown by measuring the resistance as a function of the time after the bombarding current was turned off. The rate of increase of resistance seemed to be very reasonably accounted for by the time required for the tube parts to cool off. In one case the entire tube was heated using external heaters. A temperature rise from 25°C to about 50°C brought about a 50 percent decrease in phosphor resistance. Determinations of the resistance of four different



FIG. 5. Hypothetical curves to explain stabilization of screen potentials.

phosphors gave 72 megohms and 1400 megohms for two fine grain samples and 6.3 megohms and 250 megohms for two coarse grain samples which were held to the glass plate by a potassium silicate binder. The wide range of variation in the resistance of these phosphors indicates that

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further study of the conduction properties of phosphors is really much needed because of the important part conductivity may play in the functioning of cathode-ray tubes operated at high voltages.

# EXPLANATION OF POTENTIAL MEASUREMENTS WITH HYPOTHETICAL CURVES

With the help of the hypothetical curves of Fig. 5, it is easy to understand the main features of the curves of Fig. 4. Let the primary beam current reaching the phosphor be  $i_p$  and the "saturation" secondary emission current be  $i_s$ . This means that the idealized secondary emission yield should be a function of the screen to cathode potential  $(V_{sc})$  and given by

$$(i_s/i_p) = y = F(V_{sc}).$$
 (1)

A likely form of this function is shown by the solid line of Fig. 5. The idealized saturation emission is to be distinguished from the *actual* secondary emission current  $(i_a)$  collected by the anode since the latter depends on geometrical factors and also on the potentials applied to the elements within the measuring tube. Of these potentials, the voltage difference between the screen and the anode  $(V_{sa})$ , will be the most important. The function  $f(V_{sa})$  shown by the dotted line at the extreme right of Fig. 5 is defined by the following relation

$$(i_a/i_s) = f = f(V_{sa}). \tag{2}$$

This function  $f = f(V_{sa})$  may be described as the fraction of the ideal secondary emission current which actually arrives at the anode. The condition which must be satisfied for a perfectly insulated screen to have a stable screen potential while being bombarded by a homogeneous beam of primary electrons is given in the following equation which is expressed in its three forms,

$$\dot{i}_p = i_a,$$
 (3a)

$$(i_s/y) = i_s f, \tag{3b}$$

$$1/y) = f. \tag{3c}$$

Eq. (3c) shows that a simple graphical method of

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visualizing the process by which the screen potential is established, will be obtained if the function (1/y) is plotted and intersections between it and a "movable" f curve are determined. The examples shown in Fig. 5 are for  $V_{ac}$  values of 350; 1000; 2000; 5000; 8000 and 10,000 volts. For these cases the intersections are seen to come at values of screen to cathode potential ( $V_{sc}$ ) of 300; 990; 1980; 4750; 6300 and 6500 volts. The differences between the corresponding values given, indicate the expected potential differences between the screen and the anode.

It is easy to see by this example why one must expect that the potential of an insulated phosphor will differ very little from that of the anode for potentials above four or five hundred volts and also why large differences in potential will develop when the anode potential exceeds that at which the secondary emission yield is unity. In the case shown this occurs at 6500 volts. After passing this point of unit yield, it is quite likely that y does not fall by more than fifteen or twenty percent as the screen to cathode potential is increased by three or four thousand volts. If conductivity or secondary emission from an auxiliary electron source which is bombarding the screen with five- or six-hundred-volt electrons, is introduced to take care of the excess electrons, then a worthwhile increase in the effective screen potential will result. It would also be of value to investigate means of increasing the normal secondary emission by the deposition of very thin surface lavers.

In order to understand the performance of a given phosphor more quantitatively, it might be of value to determine by direct measurement the form of the curve  $F(V_{sc})$ . It could be done by bombarding the surface with two independent electron guns so well designed that a reasonably uniform beam of accurately measurable intensity could be focused on to a small circular glass target with probe wires so as to use the electrometer method of measuring the screen potential. By finding combinations of beam intensity and beam energy which keep the phosphor test plate at definite potentials relative to the cathode or the anode, it should be possible to obtain quite an accurate determination of the true secondary emission vield  $F(V_{sc})$ .



FIG. 6. Log of light output as a function of log of current density.

# Phototube Construction for Luminosity Measurements

A commercial photoelectric cell was set up to measure the light output from the phosphor but this attempt failed for two reasons. The light output from the filament produced a photocurrent many times larger than that due to the luminosity of the phosphor when an intense electron beam was used. The difficulty could have been eliminated by using a filter to cut off all of the infrared sensitivity. This was not done because experiment showed that the "dark current" was so great that the cell could not be used for the weaker intensities of light and it was clearly necessary to measure these weak intensities if the work was to be of value. The second trial was made with a potassium photoelectric cell made by condensing the metal on the inside of a small spherical glass bulb.4 The anode was supported on a well insulated side tube. From the standpoint of sensitivity and freedom from "dark current" this tube was perfectly satisfactory. A new difficulty developed which is mentioned here in order to put other experimenters on their guard when using similar tubes for measuring very weak light intensities.

<sup>4</sup> W. B. Nottingham, J. Frank. Inst. 205, 637 (1928).



FIG. 7. Light output as a function of current density. See Fig. 6 for symbols.

In making one of these tubes it is inevitable that a few droplets of potassium will become detached from the main body of potassium forming the photoelectric cathode on the inside wall of the tube. These droplets, generally at the boundary line of the window or at the beginning of the insulated support of the anode, charged up positively and reached anode potential after which they became inactive as photoelectric emitters. If the current measured was large, then these islands of emission surface were quickly charged and the cell operated quite normally with no apparent trouble. If the current was small an apparent "fatigue" was observed since the islands at first contributed to the photoelectric current for a time depending on the intensity of the light. Some time was required for the islands to return to cathode potential after the light was cut off. This restored the cell to full sensitivity and the process could be repeated. These changes in photoelectric current were observed and at first attributed to a "fatigue" effect in the phosphor. The true explanation of the effect was discovered and a new phototube constructed which was entirely free from any such difficulty.

The new photoelectric cell was made by mounting a tantalum "pill box" 3.8 cm in diameter and 4.0 cm high on a single lead tungsten-to-glass seal. The box had two openings of which one was in one end and the other in the

middle of the side of the cylinder. The latter served as the window to admit the light and since the opening was one centimeter square it was covered by a "grid" of fine tantalum wires spaced about 0.1 cm apart. The anode was made from a tantalum strip 0.5 cm wide and 4 cm long and was bent in the form of a springy hoop and welded to a second single lead seal. The opening in the end plate of the "pill box" was made in the center and was just large enough to permit the anode to slide in when squeezed. A rather open seal-off constriction was attached to the glass envelope so as to point directly through this hole in the end plate. The axis of the constriction made an angle of about forty degrees with the axis of the tube. The anode seal was reentrant and about ten centimeters long so as to allow plenty of room for a long external leakage path and a guard ring which also furnished the means of supporting the tube. After the tube was thoroughly baked and the tantalum box outgassed, potassium which had been carefully distilled was shot through the constriction to give a good coating of clean potassium inside the "pill box."

The phototube was carefully shielded so that no induced charges would affect the measuring system when large changes in potential were made at the main tube. The entire system was also shielded to reduce the effect of outside disturbances and to eliminate all stray light. The photoelectric currents were measured by determining the drop produced by the current over a high resistance. A series of these were used varying from 10<sup>8</sup> ohms to 1.5×10<sup>10</sup> ohms. An FP-54 tube used with a DuBridge-Brown<sup>5</sup> circuit served as the indicator to show when the "IR" drop was exactly balanced out by a measured e.m.f. With the amplifier sensitivity used of 5 mm per millivolt, a photoelectric current of 10<sup>-13</sup> amp. could be measured with the required accuracy.

# LIGHT OUTPUT AS A FUNCTION OF CURRENT DENSITY

Although it is often assumed that the light output from a phosphor is directly proportional to the current density when the area covered and the bombarding electron energy are constant, the

<sup>5</sup> L. A. DuBridge and H. Brown, R. S. I. 4, 532 (1933).

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work of Levy and West<sup>6</sup> as well as the present study shows that there is a definite saturation effect as the current density is increased. The published data of Levy and West cover a wide variety of phosphors but show results for only one voltage and also there is some question as to the accuracy of their results at low intensities since the curves, which are plotted on a linear scale, do not pass through the origin of the graph.

The data here presented suffer from the fact that they apply to only one type of phosphor, namely willemite, but on the other hand they cover a very wide range of intensity and a wide range in voltage. The results shown in Fig. 6 are typical of many curves taken on a number of different samples of willemite obtained from different sources. In order to explain the method used in plotting Figs. 6 and 7, it will be necessary to anticipate a result which will be discussed in considerable detail in the next section of this paper. Over the low voltage range for all phosphors and over the entire observable range for some phosphors, the following empirical equation has been found<sup>7</sup> to represent the observed data with accuracy.

$$L = Q(i) \cdot (V_{sc} - V_0)^2.$$
 (4)

Here L is the light intensity,  $V_{sc}$  is the screen to cathode potential,  $V_0$  is a constant which might very well be called the "dead voltage," and Q(i) is a function of the current density which, according to these experiments, is the same for all samples of willemite tested. For the particular sample from which the data shown in Figs. 6 and 7 were obtained, the "dead voltage" Vo was found to be zero and therefore a plot of  $(L/V_{sc}^2)$  as a function of the current density (i) gives a graphical representation of the function Q(i) as shown in Fig. 7. The method of plotting used in Fig. 6 is in many ways more instructive since the use of "log" scales for both the abscissa and the ordinate brings out the true nature of the function in a striking manner. Over a very wide range of current density below 2.5 microamperes per sq. cm the light output was accurately directly proportional to the current density as shown by Fig. 6, since the experimental points fall along the straight line of unit slope which may be extrapolated as far into the high current region as needed. If the observed points fall below this line a saturation effect is indicated. We may define the expression relative "efficiency" as the ratio of the observed light output at any specified current density to that read on the straight line at this same current density. With this definition we see that at 20 microamperes per sq. cm the "efficiency" has dropped to 65 percent. Another way of stating it is that 35 percent of the light which one might expect to obtain is lost due to some saturation effect. As will be shown later in this paper the "efficiency" drops to about two percent when the current density is increased as high as ten milliamperes per sq. cm (see Fig. 14).

If Eq. (4) is written in the logarithmic form as follows,

$$\log_{10} L = \log_{10} Q(i) + \log_{10} V(V_{sc}), \tag{5}$$

it is clear that when the voltage is held constant, plots of  $\log_{10} L$  against  $\log_{10} i$  will superpose on each other if the saturation for a given phosphor is independent of the bombarding voltage. Nearly one hundred sets of measurements have been made on nine different samples of willemite at screen voltages from 500 to 6500 volts, and in all cases the function Q(i) was the same within the experimental error. The difficulty of determining the "absolute" current density was the largest source of error and this is thought not to exceed ten or fifteen percent. Relative measurements were all accurate to within about two percent.

It is very surprising indeed that the function Q(i) should be the same for all of the samples of willemite because there certainly must have been considerable difference in the concentration of "activator" present and also a difference in the state of strain in the various cases because of differences in heat treatment used in preparation. It is hoped that a systematic study can be made of this saturation effect since it is quite likely to be of importance from the standpoint of a more complete understanding of the atomic processes involved and also from the practical point of view since an increase in luminous output of ten or twenty to one at the very high current densities is not too much to hope for if this saturation loss can be greatly reduced.

Although there are important advantages in

<sup>&</sup>lt;sup>6</sup> L. Levy and D. W. West, J. I. E. E. 79, 11 (1936).

<sup>&</sup>lt;sup>7</sup> W. B. Nottingham, Phys. Rev. **51**, 591 (1937) and Phys. Rev. **51**, 1008 (1937).



FIG. 8. Light output as a function of the bombarding energy in volts. Moderately fine grain zinc orthosilicate.

the use of the photoelectric cell for accurate measurements of light intensity, there are also certain limitations in its use. In the first place it is generally necessary to use one of the standard visual methods of measurement in order to convert the photoelectric current values into luminosity units. This can be done under conditions most favorable for accurate measurements with the illuminometer which one chooses to use and then the photoelectric cell can be utilized to make rapid and accurate relative measurements over a very wide range in intensity. In general it is very necessary that there be no change in the spectral quality of the light. This is especially important when the range of wavelengths used falls in a part of the spectrum over which the sensitivity of the cell changes very rapidly with wave-length as is the case when a potassium photoelectric cell is used to measure the green light emitted by willemite under electron bombardment. It is generally assumed that the true spectral distribution found in the light emitted is independent of the electron energy and

current density and no evidence was found in these studies to indicate the contrary. In case this work is extended an attempt will be made to test this point since the results depend very definitely on the truth of this assumption.

# LIGHT OUTPUT AS A FUNCTION OF ELECTRON ENERGY

The Lenard<sup>8</sup> law for the variation of luminosity with electron energy is

$$L = (1/C) \cdot Q \cdot (v - v_0), \qquad (6)$$

where C is a constant, Q the "beam" intensity, v the electron energy and  $v_0$  the "dead" voltage. This law has been used extensively as a practical empirical equation as for example by Leverenz<sup>9</sup> and does serve to represent a limited range of some observed data especially when the anode potential is used as a measure of the electron energy instead of the true screen potential. The work of Levy and West<sup>6</sup> shows that the candlepower increases more rapidly than the first power of the voltage although they do not make a detailed analysis of their data. An investigation by Brown<sup>10</sup> led him to conclude that for the electron energy range up to about 800 volts, the brightness B is given by the formula  $B = KJV^2$ where K is a constant. J the current density, and V the anode potential. This formula is a special case of that given in Eq. (4) which was arrived at quite independently.

The procedure found most convenient in these studies involved the observation of the luminosity as a function of the current while the potentials of all electrodes were maintained constant. For a given sample this was done at quite a number of voltages on the second anode generally between 500 volts and 8000 volts. The voltage on the first anode relative to the second was adjusted so as to bear a constant ratio to the voltage  $V_{ac}$  of either 0.2 or 0.02. This was necessary in order to keep the electron trajectories the same at all voltages. An individual set of points shown in Fig. 6, will serve to illustrate the kind of experimental data obtained although the photoelectric current was plotted as a function of the current to the second anode instead

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 <sup>&</sup>lt;sup>8</sup> P. Lenard, Ann. d. Physik, **12**, 449 (1903).
<sup>9</sup> H. W. Leverenz, J. O. S. A. **27**, 25 (1937).
<sup>10</sup> T. B. Brown, J. O. S. A. **27**, 186 (1937).

of using the photocurrent divided by the square of the screen potential as in Fig. 6. For each voltage studied, the light intensity per unit anode current was obtained by reading off the value of photoelectric current found on the straight line of unit slope on each plot at a specified value of anode current such as one microampere. The table of values thus prepared served as the basis of plots similar to those of Figs. 8 and 9. The results presented in Fig. 8 are for an RCA zinc orthosilicate with an average grain size thought to be about  $2 \times 10^{-4}$  cm in diameter supported on glass without binder. The range in voltage used on the second anode for this set of data was from 600 volts to 8000 volts. With an anode voltage of 8000 volts the screen potential was observed to be 1550 volts negative with respect to the second anode. This large difference in potential between the screen and the anode caused a reduction in the proportion of the primary beam which arrived at the test surface. Early in this investigation, it was recognized that a correction of this kind would have to be made whenever large differences in potential developed between the screen and the anode and for this reason a tube was constructed with a carefully built Faraday cage located in the aperture usually occupied by the phosphor test plate. In spite of the care used in the design of the cage secondary emission from the cage made it impossible to measure the



FIG. 9. Light output as a function of bombarding energy in volts. Very fine grain zinc orthosilicate.

spreading effect on the primary beam brought about by the difference in potential between the cage and the second anode when high voltages were used. As the second anode voltage was reduced to less than fifty volts curves taken were found to approach a limiting curve which was independent of the actual voltage but depended only on the voltage ratios used. Two curves taken at twenty and thirty volts were identical. Corrections thus arrived at and used in connection with the data in Figs. 8 and 9 are tabulated in Table I.

11	10.00			1 T
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PRIMARY BEAM STRIKING SCREEN	$V_{sa}/V_{ac}$
1.0	0
0.9	0.1
0.83	0.2
0.77	0.3
0.71	0.4
0.65	0.5

Later an attempt was made to test this correction curve by depositing a very thin layer of phosphor on a conducting plate and using the variation of the light emitted as a measure of the spreading of the electron beam when the screen to cathode voltage was constant and the second anode voltage varied. The test was not satisfactory because of the poor alignment of the filament. Unfortunately it was not possible to repeat this experiment although it would no doubt give more reliable results than the Faraday cage method used.

The straight line through the points of Fig. 8 is drawn with a slope of *two* with no correction for "dead" voltage. The fact that such a correction is logical and is related to the average surface condition of the grains of the phosphor was illustrated by experiments with a coarse grain phosphor which was held to the test plate by a considerable amount of potassium silicate put on to find out what effect it might have. In this case the "dead" voltage turned out to be 450 volts. This was found in two ways. First the light intensity per unit beam current was plotted as the ordinate on log-log paper and the screen potential was plotted along the abscissa. The curve thus produced had a slope of the order of



FIG. 10. Diagram of circuit used with RCA C-730 tube investigation.

three or four at the lower end and approached a slope of two at the upper end. "Dead" voltage corrections of 400, 450, and 500 volts were tried and it was found that the 450 volt correction gave the best straight line and at the same time the slope of the line was very nearly two. If one had a good reason to believe that Eq. (4) had the correct form theoretically, then the best way of finding a good value of the constant V<sub>0</sub> would be to plot the square root of the light per unit beam current as a function of the screen potential and determine the intercept on the voltage axis. This method was also used in this case and  $V_0$  was found to be 450 volts as expected. The fact that the constant  $V_0$  respresents an average property of the phosphor was brought out by studies of this surface which had such a high "dead" voltage. Although the light output for voltages below 450 volts was so weak that it could not be measured with the photoelectric system used, it was observable by eye down to about 300 volts.

The results shown in Fig. 9 are for a very fine grain phosphor. The average grain size was thought to be about  $3 \times 10^{-5}$  cm in diameter. Such small particles are difficult to measure and

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it is possible that some of the grains were four or five times smaller than this and some were certainly three times larger. This phosphor was deposited by the "drop" method from a milk-like suspension of the material. The analysis again showed that the light intensity increased with the square of the screen potential for voltages below 3000 volts but for voltages above this the light output increased as the 1.41 power of the electron energy expressed in volts. It is interesting to note that the penetrating power of threethousand-volt electrons is  $2.25 \times 10^{-5}$  cm for Zn<sub>2</sub>SiO<sub>4</sub> according to the calculations of Leverenz.9 On the basis of the small evidence so far obtained it is not possible to draw conclusions with certainty but one can see that the indications are that the light output from a phosphor increases as the square of the bombarding voltage unless the surface layer of the phosphor grains is disturbed in the grinding process or is covered with some impurity such as a silicate binder. This rule seems to hold for all phosphors studied up to the highest voltages obtainable depending on the secondary emission properties of the grain, if the bombarding energy is not sufficient to penetrate completely the individual grains of the phosphor.

# Screen Potentials and Luminosity Measurements as Found by Using an Experimental Nine-Inch Cathode-Ray Tube<sup>11</sup>

The C-730 tube has an electron gun with an indirectly heated cathode, a control grid, an inner anode maintained at a constant potential, and an outer anode known as the "first anode" of the tube. A conducting coating on the inside of the tube is known as the "second anode." The focusing of the electron beam depends almost

<sup>&</sup>lt;sup>11</sup> The results discussed in this section were obtained by using an experimental model of a nine-inch cathode-ray tube with the numerical designation C-730 which the Research and Engineering Department of the Radiotron Division of RCA Manufacturing Company very kindly loaned me for the time required for these tests. The results should not be taken as in any way representative of expected performance of this type of tube but must be understood to apply to this particular tube. The reason for publishing this information as it stands is that it brings out the relationship existing between many of the fundamental properties of phosphors disclosed by the investigations reported above and the performance of a phosphor in a tube of a practical design.

entirely on the ratio of the first and second anode potentials, and the intensity of the beam is governed by the potential of the control grid. Preliminary experiments using magnetic deflections and also tests of the current characteristics as observed at each collector in the tube, seemed to indicate that its performance was remarkably free from any disturbing influence of either unwanted secondary emission or gas effects. Dr. Herbert Nelson<sup>12</sup> of the Radiotron Division of the RCA Manufacturing Company, has experimented with the problem of determining the screen potential in a tube of this kind by painting a disk of "aquadag" on the outside surface of the glass and then while the glass was heated to a temperature of two or three hundred degrees centigrade by means of a hot air blast he found the potential relative to the second anode at which the disk had to be maintained so that no current flowed through the glass from the phosphor to the disk.

A diagram of the circuit used for the study of the screen potential as a function of current density and second anode voltage is shown in Fig. 10. A Compton electrometer was used to measure the currents received by the "aquadag" contact on the outside of the tube. Three contacts were made near the center of the screen area of the tube. The innermost one was a circle 0.6 cm in diameter filled in solid with "aquadag" and around this were alternate rings of nonpainted and painted surface each one of which was 0.5 cm wide. This system of two conducting rings and a center formed a target like arrangement of contacts and by means of a weak bar magnet the electron beam was deflected so as to strike near the center of the "bullseye" when the beam was focused.

With a constant bombarding voltage of 2000 volts and a beam current of  $120 \times 10^{-6}$  amp the electrometer current was measured as a function of the voltage and the slope of the curve showed the effective resistance of the Nelson "heat-contact" to be 7500 megohms when a moderate blast of hot air was used. This could be reduced to 1000 megohms by increasing the temperature of the blast. Since the electrometer was suf-

ficiently sensitive so that the lower temperature blast was perfectly satisfactory, this was used for all of the measurements to be described below.

The measurements made with the second anode voltage at 8000 volts were in some ways the most striking and are therefore shown in Fig. 11. With 1000 volts on the first anode the diameter of the beam at the screen was about 1.7 cm and the difference in potential between the "aquadag" and the second anode was only 55 volts with  $270 \times 10^{-6}$  amp. beam current. (See curve A.) With a beam current of  $160 \times 10^{-6}$ amp. the difference in potential was 44 volts. The current densities for these two cases compute out to be  $120 \times 10^{-6}$  and  $70 \times 10^{-6}$  amp. per sq. cm. As the potential on the first anode was increased, the electron beam came to a focus and then diverged again. At the focal point, the current densities for curves A and B of Fig. 11 were about  $5 \times 10^{-3}$  and  $3 \times 10^{-3}$  amp. per sq. cm, respectively and the potential differences were 1350 and 690 volts. Measurements with still higher current densities gave a limiting difference in potential of 1650 volts. It seems certain from these results as well as from observations taken with a wide range of lower second anode potentials that not all of the beam current is taken away from the screen by simple secondary emission. An obvious means at hand is that of conductivity through the screen to the second anode which is in contact with the phosphor.

The resistance R of a thin sheet of conducting



FIG. 11. Variation of "screen" potential with first anode or focusing voltage. Second anode voltage constant at 8000 volts. Curve A, grid -10 volts, beam current from  $270 \times 10^{-6}$  to  $375 \times 10^{-6}$ . Curve B, grid -15 volts, beam current from  $160 \times 10^{-6}$  to  $225 \times 10^{-5}$ .

<sup>&</sup>lt;sup>12</sup> The results of Dr. Nelson's extensive investigations with the "heat contact" which he devised are to be published in the near future.



FIG. 12. Anode to screen potential as a function of current density. Curve A, 7000 volts on second anode. Curve B, 8000 volts on second anode.

material of uniform resistivity  $\rho$  which is in the form of a ring of inside radius  $r_1$  and outside radius  $r_2$  is given by the formula

$$R = (\rho/2\pi) \cdot \ln (r_2/r_1).$$
 (7)

The resistivity  $\rho$  is expressed in ohms and is the resistance across a square of any size since the resistance of such a surface is assumed to be proportional to the distance between the contacts along two sides of the square and inversely proportional to the length of the sides along which contact is made. If the resistivity of the screen were assumed to be 25 megohms, then for the case described above for which the beam diameter was 1.7 cm the resistance of the screen from the periphery of the beam to the second anode would be 10 megohms. With 55 volts as the difference in potential,  $5.5 \times 10^{-6}$  amp. would flow through the screen to the anode. This would be only two percent of the beam current. If the focused beam had a radius of only 0.02 cm the resistance of the screen would rise to only 25 megohms and yet the screen potential increased to 690 volts for curve B and 1350 volts for curve A. The assumption of a resistivity as low as 25 megohms was made in order to make the calculations as favorable as possible in support of the conductivity hypothesis. These calculations seem to show that direct conductivity to the second anode cannot be responsible for the great change in screen potential with increasing current density.

Two other possibilities seem to be worth further consideration which are first an assumed nonuniformity in the secondary emission properties of the surface. In this case the "active"

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secondary emission areas would receive electrons from the less active regions by conductivity which would give rise to a considerable difference in potential from one small region to another over the surface. The experiments so far performed give no corroborating evidence in support of this hypothesis. A second possibility is that there is a space charge effect at the surface of the phosphor since the secondary electrons have relatively small initial velocities and might require a large difference in potential between the focal point and the second anode in order to accelerate these electrons away. Again this hypothesis does not quite fit the facts as illustrated in Figs. 12 and 13.

Figure 12 shows curves A and B which represent, for 7000 and for 8000 volts on the second anode, the difference in potential between the screen and the second anode as a function of the current density. Because of the difficulty of measuring the area of the spot on the screen in the very short time during which the beam was permitted to bombard the surface and also because of the nonuniformity in the distribution of current over the beam, the points serving as the basis for the curves of Fig. 12 were rather scattered and yet it is thought that these curves are nevertheless worth reporting. The curve given in Fig. 13 bears such a complete resemblance to those of Fig. 4 that one is tempted to conclude that this represents the true behavior of the phosphor when not complicated by the complex phenomena which are responsible for the great change in screen potential as the current density in the beam is decreased. This conclusion cannot be made with reasonable certainty without further investigation.

The potassium-on-tantalum photoelectric cell, described above was used to measure the light output from the C-730 tube. A region not far from the center of the screen was selected which was free from imperfections in light distribution over the area of the beam. Here a circular opening one square centimeter in area was defined by painting "aquadag" on the end of the tube. A short focal lens was used to receive the light and focus it on the window of the photoelectric cell. Between the lens and the screen a mirror was mounted on a support so that it could be swung into place directly in front of the circular opening



FIG. 13. Screen to anode potential as a function of the second anode potential for very high current densities.

painted on the glass and in this way it was possible to adjust the size of the beam to fill the opening exactly and also properly center it. The thickness of the glass was so great that it was impossible to locate the beam properly without the use of the mirror. With the voltage on the second anode constant, the light output was measured as a function of the current in the beam. The current to the second anode thus indicated the current density directly since the cross-section area was maintained constant at one sq. cm. For each different voltage the light output was plotted as a function of the current density on log-log paper. These curves were found to superpose on each other to within the accuracy of the experiments again indicating that the saturation effect found in the previous studies depended only on the current density and was independent of the bombarding electron energy. Measurements made using higher electron densities and a smaller beam diameter fit in also with the data using the standard one sq. cm spot size. All of the results are therefore combined together in Fig. 14. The solid line was drawn through the points which numbered about a hundred in all and the two dash lines were drawn so as to include all of the observations between them. Most of the points taken were for current densities less than  $5 \times 10^{-4}$  amp. and therefore the lower part of the curve can be said to be more certain than the part above  $5 \times 10^{-4}$ amp. which was determined by only six points. The data shown in Fig. 6 agree within the experimental error with the curve of Fig. 14. There is little doubt but that current densities of the order of 10<sup>-2</sup> amp. per sq. cm will be used in practical tubes and if this experience is at all universal then such tubes will be operating at

an efficiency far below what one might reasonably hope for. Fig. 14 shows that 98 percent of the light is lost due to the saturation effect for this particular phosphor at a current density of  $10^{-2}$  amp. per sq. cm.

Figure 15 illustrates the results obtained for the variation of light output with second anode voltage.

These data were taken by observing the light output as a function of the current density at different voltages and then after plotting these data as described above, the light output per unit current density was determined by selecting a point on the straight line portion of the log-log plot. It was noticed that after the screen was severely bombarded at high voltage and high current density, the light output with a standard low voltage and low current condition was observed to decrease. For this reason a systematic study of the light output as a function of the voltage was not undertaken using the region of the screen originally selected but another was found which had not been bombarded so strongly. The current densities used on this second one square centimeter circular opening were not allowed to exceed 10<sup>-5</sup> amp. per sq. cm. The first run was made at 3000 volts on the second anode and after this ten more runs were made at lower



FIG. 14. Light output as a function of current density. Individual curves for all voltages from 500 to 9600 volts superimposed by vertical shift only.



FIG. 15. Light output per unit current density as a function of the bombarding electron energy. Circles for initial operation at voltages below 3000 volts, dots show change in light output after high voltage bombardment.

voltages down to 500 volts. These results were accurately reproducible and are represented by the circles of Fig. 15. Following this runs were made at higher voltages and then a run was made at 1700 volts. This point shown by a dot is obviously below the value expected by interpolation by about 25 percent. More low voltage data were taken and although these were again reproducible, the results obtained in the transition region between 1000 and 2000 volts showed that a permanent change had been undergone by the phosphor. The two straight lines drawn through the points of Fig. 15 have 2.0 and 1.2 for their slopes and thus confirm the previous results illustrated by Figs. 8 and 9 that for low electron energies the light output increases with the square of the bombarding voltage. The reason for the failure of this rule above about 1500 volts should be investigated further since an increase of some five- to tenfold in the light intensity could be obtained if by using a larger grain size for example the range of application of the "square law" could be extended.

A possible explanation for the change in the rate of increase of light output with voltage is that a voltage difference between the screen and the anode was developing at the higher anode voltages in spite of the fact that the measurements using the Nelson "heat contact" showed that very little difference in potential should exist for these low current densities even up to the highest voltages used. Since the screen potential measurements were made with the glass and the screen hot, it was considered worth while to observe the effect of the application of the hot air blast on the light output. With 9600 volts on the anode, an increase in temperature first caused a 25 percent increase in the light while a further increase in temperature reduced the light output to 10 percent below that observed at room temperature. The same effect was observed to a less marked degree at 8000 volts. These experiments thus turned out to be inconclusive because of the complex nature of the phenomena involved and again indicate the importance of pursuing the investigation further.

The author's most sincere thanks are hereby extended to the members of the staffs at both the Harrison and the Camden laboratories of the RCA Manufacturing Company who have assisted so extensively with these studies and especially to Dr. V. K. Zworykin, Dr. G. R. Shaw, and Dr. L. B. Headrick. I am also indebted to Dr. A. W. Hull and Dr. G. R. Fonda for the opportunity of discussing the results with them. For the faithful technical service and assistance rendered, I owe much to Messrs. J. Ryan, L. W. Ryan and A. B. White.







# Electrical and Luminescent Properties of Willemite Under Electron Bombardment

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# Electrical and Luminescent Properties of Willemite Under Electron Bombardment

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An insulated surface uniformly bombarded with electrons of a given energy attains a potential relative to other elements in a high vacuum tube such that exactly as many electrons leave the surface by secondary emission as there are primary electrons arriving. A tube and circuit have been constructed for determining accurately this potential for willemite surfaces while being bombarded by electrons of energy range up to 10,000 volts. It was found that the surface potential was only slightly negative with respect to the most positive anode of the tube over the lower range of energy but finally reached an upper limit of potential relative to the cathode usually between 6000 and 7000 volts. The resistance between wires covered by the willemite was found to be independent of the bombarding current and voltage except in so far as this bombardment changed the temperature of the material. A special potassium phototube is described which was used to determine the light output from the bombarded surface as a function of the current density and the electron energy. The light was found to be accurately proportional to the current for densities below  $2.5 \times 10^{-6}$  amp. per sq. cm but above this a saturation effect set in quite gradually so that with a current of  $20 \times 10^{-6}$  amp. per sq. cm the light output was

#### INTRODUCTION

MATERIALS which luminesce under electron bombardment have been used in "electron projection" tubes by Johnson and Shockley<sup>1</sup> and others to study the electron emission from hot filaments by accelerating the electrons from the filament to a coaxial glass cylinder coated internally with a luminescent substance. In order to make these thermionic studies more quantitative, we needed to know more about the electrical and luminescent properties of the phosphors used and therefore undertook what was originally intended to be a brief investigation along this line. The results obtained

 $^1\,\mathrm{R.}$  P. Johnson and W. Shockley, Phys. Rev. 49, 436 (1936).

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only 65 percent of the value which it would have been had the light intensity per unit current density remained constant. The light output for a constant current was found to increase with  $(V - V_0)^2$  where  $V_0$  is the "dead voltage" when the bombarding energy was less than that required to penetrate through the individual grains of the willemite. An experimental nine-inch cathode-ray tube was also studied for screen potential and light output as a function of current density and anode voltage. The difference in potential between the screen and the anode was again small for the lower range in voltage but with anode voltages above 7000 volts, the apparent screen potential depended on the current density so that a change of potential of the screen of as much as 1500 volts was observed as the current density was increased from one to ten milliamperes per sq. cm. The light output increased with the square of the bombarding potential up to 1500 volts but above this it increased with the 1.2 power of the voltage. The light output per unit current density observed at 10<sup>-2</sup> amp. per sq. cm was only two percent of that observed at 10<sup>-6</sup> amp. per sq. cm on account of the severe "saturation" effect found at high current densities.

seem to be of sufficient general interest to warrant their publication in spite of the fact that the tube design would have to be improved before one could maintain that the results were entirely free from possible adverse criticism. Since it would require a longer time to make the necessary improvements than there will be available to the writer in the near future, it has been thought best to bring forward the results which are available to date with the hope that the work will be extended and made more quantitative in this laboratory or some other.

# **OBJECTIVES**

It is obvious that the potential of a phosphor, when under electron bombardment, will adjust itself relative to the other elements of the tube so that there will be no accumulation of charge. If the phosphor is entirely insulated, either secondary electron emission or the arrival of positive ions or both of these processes must be invoked to keep the potential constant. In "sealed-off" tubes the effect of the ions can be made entirely negligible. The first objective therefore was the investigation of secondary emission properties of certain phosphors. Since in most practical applications it is possible to make contact with the phosphor either by supporting it on conducting material or by making contact at the edge, the second objective was to determine the resistivity of phosphors under operating conditions.

With the potential of the luminescent material known, it is clear that the third and fourth objectives of this study would naturally be the determination of the light output as a function of the true bombarding potential of the phosphor relative to the cathode and as a function of the current density.

#### TUBE AND CIRCUIT DESIGN

The sketch shown in Fig. 1 shows the essential parts of the tube used. This drawing has been prepared to illustrate certain features of construction rather than attempt to draw an exact reproduction of the tube. Seven single lead tungsten-to-glass seals were arranged around the end of a large Pyrex "test-tube" with a bottom view lay-out as shown in Fig. 1b. A side tube with a short tungsten seal for mounting the "getter ring" was sealed as shown in Fig. 1a, and the blank thus prepared was connected to an exceptionally good vacuum system for the preliminary baking of three or four hours at 500°C. This served to anneal the glass partially and give the seals a rigorous test since the oven was allowed to cool very slowly after this bake. The blank was then cracked open by using a hot wire at the point marked "crack-off" and the metal parts which had all been vigorously heat treated in a separate blank were assembled as shown. The parts were carefully aligned so as to be concentric and the slits 1 and 2 properly located.

Two "fernico" wires 20 mils in diameter and 10 cm long were imbedded in small tubes of 705-AO glass. At one end, these were in turn melted into a small plate of this glass which was finally ground to form a flat rectangular plate 0.55 cm by 0.95 cm with short sections of the "fernico" exposed as shown in Fig. 1c. The phosphor was applied to this surface by one of the following three methods. (1) An air operated spray gun was used for the moderately fine grain phosphors which were suspended in acetone. The grains were sufficiently course so that constant agitation by air bubbling was needed to keep the phosphor in suspension. The spray was operated in this way until the coating was thick enough to hide completely the "fernico" wires lying in the surface of the test plate. (2) The very fine grain phosphors were furnished to me in the form of a "milk-like" suspension in acetone. In this case the grains were so fine that some hours were required for the phosphor to settle out after the suspension had been agitated. The grain size was estimated to average approximately  $3 \times 10^{-5}$  cm



FIG. 1. (a) Sketch of tube. (b) Bottom layout of tube blank. (c) Test plate with "fernico" wires exposed in surface.

in diameter. It was found quite practical to place a single drop of this suspension on the test plate and allow the acetone to evaporate thus leaving a uniform and well adhering coating of the phosphor. (3) Still a third method used for very coarse grains utilized a water solution of potassium silicate for a binder.

After the test sample was prepared, movable glass sleeves were slid over the two glass-covered wires which formed the support of the test sample. These wires were welded to the tungsten leads marked  $P_1$  and  $P_2$  in Fig. 1 in such a manner that the test plate fitted into the 0.6 cm by 1.0 cm opening in the second anode shown as  $A_2$ . After the welding was completed the glass sleeves were adjusted to cover the welds completely. These sleeves were formed so as to fit very closely over the glass-covered "fernico" wires and also over the glass of the tungsten-to-glass seal. It was very important that no part of the test plate leads be exposed to the direct arrival of electrons since the method used to study the electrical properties of the phosphor depended on the assumption that no charges could flow into the test plate connections except those which flowed through the phosphor.

A thoriated tungsten filament which had been polished smooth by grinding was used as the source of electrons because experience has shown that this type of filament emits electrons very uniformly after prolonged activation at about 1960°K subsequent to giving the filament the usual high temperature flashing at 2850°K. It was also possible, with this type of cathode, to open the tube as many times as desired to change the phosphor sample and at the same time not impair in any way the emission properties of the filament. Of course the filament had to be reactivated but this could be done with the same degree of perfection as often as was needed.

The four cylinders used for the first anode  $A_1$ , the second anode  $A_2$  and the guard rings  $G_1$  and  $G_2$  were made from annealed 3 mil sheet tantalum and supported on tantalum wires so that these parts could be heated nearly to a "white-heat" by electron bombardment and induction heating. Short pieces of outgassed nickel were used to assemble these metal parts to the tungsten leadin wires. Eight to ten aluminum-barium getter pellets<sup>2</sup> were welded in the form of a ring and mounted in the side-tube shown in Fig. 1. This construction was used because of the ease with which this unit could be cracked off to be cleaned and replenished with getter each time a new phosphor sample was put in the tube.

After the tube was completely assembled and sealed back together at the "crack-off," the exhaust schedule lasting between ten and thirty hours was started. After a one-hour bake at 500°C and about three hours at 470°C, during which time the liquid-air trap and the connection between it and the tube were also baked at the same temperature, liquid air was put on the trap and following this the "tube oven" and the "connection oven" were removed. The filament was then flashed and activated and the bombardment of the anodes begun. This was continued until a vacuum of the order of 10<sup>-8</sup> mm of mercury was obtained with the first anode nearly at a "white-heat" and the getter ring at as bright a red as was considered the maximum which would not explode the getter. During the early stages of heat treatment it was found that the gas given off, rapidly deactivated the filament as indicated by a considerable decrease in electron emission. The time required to bring about this deactivation served as a better indication as to the condition of the tube than any measurements which could have been made with an ionization gauge. The tube was operated at about ten times the normal maximum load during this heat treatment in that ten to fifteen milliamperes of electron current flowed from the filament to the anodes with a difference in potential between the filament and these collecters of 10,000 volts. Most of the heat thus developed was radiated by the first anode and therefore the outer electrodes  $A_2$ ,  $G_1$  and  $G_2$  were heated red hot by high frequency induction currents. The heat treatment of these outer elements was limited because it was feared that the glass test plate might melt. When it was found that under these conditions the filament remained well activated for a period of an hour or so, the seal-off capillary was softened and the getter ring heated to explode the

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<sup>&</sup>lt;sup>2</sup> Type C-400 barium-aluminum getters very kindly furnished by King Laboratories, Syracuse, N. Y., were found to be particularly satisfactory since they will withstand baking at 500°C for long periods of time without appreciable evaporation before firing.

getter. The tube was finally sealed off after another hour or so of heat treatment and pumping. After this rather vigorous exhaust schedule, the tube could be operated indefinitely at 10,000 volts with as much as one milliampere of current to the anodes without appreciable loss of activity of the cathode surface.

The diagram of the electrical circuit used for this study is shown in Fig. 2. Three power-packs using full-wave rectifiers and adequate filtering were connected as shown. Pack  $(Pa_2)$  maintained the required voltage difference between the second anode and the filament while pack  $(Pa_1)$ was used to maintain the first anode at any potential, relative to the second anode, that was needed. These power-packs and also the filament batteries were well insulated from ground. A third pack  $(Pa_g)$  was used to establish the second anode at any desired potential relative to ground. The test wires connected to the phosphor were always at ground potential as can be seen from the circuit diagram.

# MEASUREMENT OF POTENTIAL AND RESISTANCE OF PHOSPHOR WHILE BOMBARDED BY ELECTRONS

The potential difference between the second anode and the cathode will be designated as  $V_{ac}$ while that between the second anode and the first anode will be given by  $V_{a1}$ . The symbol  $V_{ag}$ will be used to indicate the potential of the second anode relative to ground. The current to the anodes was controlled by varying the temperature of the filament. Although in general the current to the first anode was set at arbitrary values between  $10^{-8}$  amp. and  $3 \times 10^{-3}$  amp., the current measured at the second anode was assumed to be directly proportional to the primary beam current. That it was necessary to make this assumption, is obviously a serious criticism of this work. Many experimental results such as the accurate proportionality between light output and current for low intensities gave "internal" evidence that this assumption was justified but none of these gave incontrovertible information. If this problem is reattacked with the aim of making it more quantitative than the present study, the tube should be so constructed that the primary beam current can be measured

directly. The fraction of the primary beam which struck the phosphor on the test plate depended to a certain extent on the ratio of the potentials  $V_{a1}$  to  $V_{ac}$  since the slit in the first anode distorted



FIG. 2. Circuit diagram.

the equipotentials and thus created an electron lens which was converging or diverging depending upon the  $V_{a1}$  to  $V_{ac}$  ratio. Whenever measurements made at one value voltage  $V_{ac}$  were to be compared with those at another value of  $V_{ac}$ , the ratio  $V_{a1}/V_{ac}$  was maintained constant. With a filament diameter of  $5.06 \times 10^{-3}$  cm and first and second anode diameters of 1.0 and 3.81 cm, respectively, the ratio  $(V_{a1}/V_{ac}) = 0.20$  gave the critical condition for an electron lens of infinite focal length at the slit in the first anode. The lens formula given by Calbick and Davisson<sup>3</sup> predicted correctly the potential ratio required to focus an electron image of the filament on the phosphor surface. This formula is  $L=4(V_{ac}-V_{a1})/(G_2-G_1)$ , where L is the focal length in cm and  $G_1$  and  $G_2$  are electric intensities in volts per cm on the inside and the outside of the first anode computed disregarding the slit.

Secondary electrons produced at the slit of the first anode or even inside this anode could strike the phosphor test surface in case it was positive with respect to this anode. If the phosphor was less than one or two hundred volts positive with

 $<sup>^{\</sup>rm s}$  C. J. Calbick and C. J. Davisson, Phys. Rev.  ${\bf 45},\,764$  (1934).

respect to the first anode these secondaries tended to charge the surface to a more negative value relative to the second anode than it would have had in the absence of these low energy secondary electrons. On the other hand if the phosphor was between three hundred and a thousand volts positive with respect to the first anode then the secondary electrons arrived at the screen with enough energy to remove more than one electron for each of these electrons received at the screen. It will be shown below that as the energy of the primary electrons is increased a value is generally reached for which only one secondary electron is produced at the screen for each primary electron which strikes it. Unless some other agency is brought in, it is impossible to make the screen more positive with respect to the cathode than this limiting value. If only ten to twenty percent of the primary electron current is removed by conducting it away through the phosphor then a considerably higher cathode to screen voltage may be attained. Still another way of discharging the screen which might be worth consideration would be to bombard it with electrons from an electron "gun" entirely auxiliary to the principle electron gun of the tube. This auxiliary gun would spray the surface of the phosphor with a copious supply of three or four hundred volt electrons and since each one of these would produce more than one secondary electron at the screen, a considerably higher voltage difference could be maintained between the screen and the cathode of the principal gun of the tube.

With the circuit shown in Fig. 2, the potential



FIG. 3. Screen potential as a function of the first anode potential showing effect of secondary emission from first anode.  $V_{ac} = 2000$  volts.

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of the insulated phosphor could always be determined with accuracy since this was obtained by adjusting the voltage of the power pack  $(Pa_q)$ to that particular voltage for which no current flowed in the electrometer circuit. Since this part of the circuit was so sensitive that a current less than 0.001 percent of the primary beam current could be measured easily, it was possible to determine  $V_{ag}$  with high precision. A necessary condition that such determinations were not faulty was that the voltage  $V_{ag}$  for zero current should be independent of the beam current and be the same for either probe wire  $P_1$  or  $P_2$  or for both of them together. In the rare cases where these tests were not satisfied, definite faults in the screen were discernible. Although the screen potential could be determined with accuracy under any particular set of conditions, the results were not always entirely free from ambiguity because of the effects of secondary emission from the first anode. A particularly striking example of the effect of secondary emission is illustrated by Fig. 3. Here the observed value of  $V_{ag}$  for zero current through the probe connections is plotted as the ordinate and the difference in potential between the first and second anodes is plotted as the abscissa. The potential of the second anode relative to the filament was constant at 2000 volts and the phosphor used for this was a zinc silicate (meta) supported by a potassium silicate binder. The resistance of this phosphor was the lowest of any measured.

The curve shown in Fig. 3 started with  $V_{ag} = 320$  volts when the first and second anodes had no difference in potential. It is certain that a negligible number of secondaries from the first anode reached the screen under this condition and therefore we can conclude that for this particular phosphor and binder, an insulated screen would charge up to a potential of about 300 volts negative with respect to the anode when the true energy of the bombarding electrons was 1700 volts. This is an abnormally large difference in potential for such low energy electrons but this curve was selected for discussion to illustrate as clearly as possible the effect of secondaries which took place as the first anode was made nearly as negative as the phosphor. At first the phosphor became still more negative with respect to the anode as it received the very low energy second-

aries which necessitated a drop in the primary beam energy from 1700 to 1600 volts in order to increase the normal secondary emission yield of the phosphor enough to make up for the arrival of the slow electrons. A discontinuity took place when  $V_{a1}$  was increased to 410 volts. The potential of the insulated screen changed suddenly over 200 volts and, with the first anode 570 volts negative to the second anode, the screen was only



FIG. 4. Potential difference between screen and second anode as a function of second anode potential. A, coarse grain phosphor with potassium silicate binder. B, very fine grain phosphor with no binder.

170 volts negative as compared with 320 volts which was the true value for the primary electrons taken alone. Under these conditions, the difference in potential between the first anode and the screen was 400 volts which further study showed to be the electron energy value giving the maximum secondary emission yield for this particular phosphor. In all of the work described below care was exercised in order to interpret the results correctly and not allow the effects of secondary emission from the first anode to invalidate the final conclusions.

The two curves shown in Fig. 4 illustrate the nature of the results obtained. These curves should be compared with that of Fig. 13 which was obtained with an experimental nine-inch cathode-ray tube with a very high current density  $(10^{-2} \text{ amp. per sq. cm})$  in the beam. The main points of interest in these curves are (1) at low voltages there is very little difference in potential between the screen and the second anode: (2) at higher voltages large differences come in and (3) a limit is reached as  $V_{ac}$  is increased such that the potential  $V_{ag}$  increases just as rapidly as  $V_{ac}$ . When this limit is reached it is impossible to obtain any increase in the bombarding electron energy by increasing the anode potential unless some other means of discharging the screen is used besides that of the simple production of secondary electrons by the primary beam. The two methods most commonly used are (1) screen conductivity and (2) the use of positive ions produced along the path of the

primary beam. As was pointed out above, a third method perhaps worth trying would be to use an auxiliary electron gun.

It is obvious from the curves of Fig. 4 that zinc orthosilicate can have very different secondary emission properties depending on the method of handling it or on the type of binder used and the kind of impurities that may be present. Curve "A" was observed with a coarse grained phosphor held to the test plate by a potassium silicate binder and curve "B" was obtained with a very fine grained phosphor put on the test plate by the "drop" method described above. One phosphor studied which happened to have a maximum attainable potential of only 5600 volts in its normal state was found to change this maximum to about 8000 volts as a result of the evaporation of a small amount of thorium from the filament on to the surface of the phosphor. The thorium evaporated over probably formed on the average less than a monatomic layer. The increase in the voltage maximum thus obtained was not permanent and the experiment was useful only to indicate that very small amounts of impurity are needed to modify the secondary emission properties very considerably.

With the circuit arrangements as shown in Fig. 2, the resistance of the phosphor could be measured when it was not being electron bombarded by measuring the current flowing around the circuit as a function of the voltage difference applied between the probe wires. The current was found to be a linear function of the voltage up to

ten volts in either direction. Tests were not made with higher voltages. In order to measure the resistance of the phosphor while it was being bombarded, it was first necessary to set the voltage  $V_{ag}$  to that value for which no current flowed in the probe wire connected directly to the electrometer. This was done with the other probe connection open. After satisfying this condition an e.m.f. of about one volt was connected between the probe wires and the current flowing in the electrometer circuit due to this e.m.f. was measured. In all experiments of this kind which were tried there was no difference in the resistance due to the bombarding electrons except in cases where the heating effect was great. In most cases it was possible to reduce the resistance to one-half its original value by heating the phosphor with electron bombardment. The fact that this was a heating effect was shown by measuring the resistance as a function of the time after the bombarding current was turned off. The rate of increase of resistance seemed to be very reasonably accounted for by the time required for the tube parts to cool off. In one case the entire tube was heated using external heaters. A temperature rise from 25°C to about 50°C brought about a 50 percent decrease in phosphor resistance. Determinations of the resistance of four different



FIG. 5. Hypothetical curves to explain stabilization of screen potentials.

phosphors gave 72 megohms and 1400 megohms for two fine grain samples and 6.3 megohms and 250 megohms for two coarse grain samples which were held to the glass plate by a potassium silicate binder. The wide range of variation in the resistance of these phosphors indicates that

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further study of the conduction properties of phosphors is really much needed because of the important part conductivity may play in the functioning of cathode-ray tubes operated at high voltages.

# EXPLANATION OF POTENTIAL MEASUREMENTS WITH HYPOTHETICAL CURVES

With the help of the hypothetical curves of Fig. 5, it is easy to understand the main features of the curves of Fig. 4. Let the primary beam current reaching the phosphor be  $i_p$  and the "saturation" secondary emission current be  $i_s$ . This means that the idealized secondary emission yield should be a function of the screen to cathode potential  $(V_{sc})$  and given by

$$(i_s/i_p) = y = F(V_{sc}).$$
 (1)

A likely form of this function is shown by the solid line of Fig. 5. The idealized saturation emission is to be distinguished from the *actual* secondary emission current  $(i_a)$  collected by the anode since the latter depends on geometrical factors and also on the potentials applied to the elements within the measuring tube. Of these potentials, the voltage difference between the screen and the anode  $(V_{sa})$ , will be the most important. The function  $f(V_{sa})$  shown by the dotted line at the extreme right of Fig. 5 is defined by the following relation

$$(i_a/i_s) = f = f(V_{sa}).$$
 (2)

This function  $f=f(V_{sa})$  may be described as the fraction of the ideal secondary emission current which actually arrives at the anode. The condition which must be satisfied for a perfectly insulated screen to have a stable screen potential while being bombarded by a homogeneous beam of primary electrons is given in the following equation which is expressed in its three forms,

$$a_p = i_a,$$
 (3a)

$$(i_s/y) = i_s f, \tag{3b}$$

$$1/y) = f. \tag{3c}$$

Eq. (3c) shows that a simple graphical method of

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visualizing the process by which the screen potential is established, will be obtained if the function (1/y) is plotted and intersections between it and a "movable" f curve are determined. The examples shown in Fig. 5 are for  $V_{ac}$  values of 350; 1000; 2000; 5000; 8000 and 10,000 volts. For these cases the intersections are seen to come at values of screen to cathode potential ( $V_{sc}$ ) of 300; 990; 1980; 4750; 6300 and 6500 volts. The differences between the corresponding values given, indicate the expected potential differences between the screen and the anode.

It is easy to see by this example why one must expect that the potential of an insulated phosphor will differ very little from that of the anode for potentials above four or five hundred volts and also why large differences in potential will develop when the anode potential exceeds that at which the secondary emission yield is unity. In the case shown this occurs at 6500 volts. After passing this point of unit yield, it is quite likely that y does not fall by more than fifteen or twenty percent as the screen to cathode potential is increased by three or four thousand volts. If conductivity or secondary emission from an auxiliary electron source which is bombarding the screen with five- or six-hundred-volt electrons, is introduced to take care of the excess electrons, then a worthwhile increase in the effective screen potential will result. It would also be of value to investigate means of increasing the normal secondary emission by the deposition of very thin surface layers.

In order to understand the performance of a given phosphor more quantitatively, it might be of value to determine by direct measurement the form of the curve  $F(V_{sc})$ . It could be done by bombarding the surface with two independent electron guns so well designed that a reasonably uniform beam of accurately measurable intensity could be focused on to a small circular glass target with probe wires so as to use the electrometer method of measuring the screen potential. By finding combinations of beam intensity and beam energy which keep the phosphor test plate at definite potentials relative to the cathode or the anode, it should be possible to obtain quite an accurate determination of the true secondary emission yield  $F(V_{sc})$ .



FIG. 6. Log of light output as a function of log of current density.

# Phototube Construction for Luminosity Measurements

A commercial photoelectric cell was set up to measure the light output from the phosphor but this attempt failed for two reasons. The light output from the filament produced a photocurrent many times larger than that due to the luminosity of the phosphor when an intense electron beam was used. The difficulty could have been eliminated by using a filter to cut off all of the infrared sensitivity. This was not done because experiment showed that the "dark current" was so great that the cell could not be used for the weaker intensities of light and it was clearly necessary to measure these weak intensities if the work was to be of value. The second trial was made with a potassium photoelectric cell made by condensing the metal on the inside of a small spherical glass bulb.4 The anode was supported on a well insulated side tube. From the standpoint of sensitivity and freedom from "dark current" this tube was perfectly satisfactory. A new difficulty developed which is mentioned here in order to put other experimenters on their guard when using similar tubes for measuring very weak light intensities.

<sup>4</sup> W. B. Nottingham, J. Frank. Inst. 205, 637 (1928).



FIG. 7. Light output as a function of current density. See Fig. 6 for symbols.

In making one of these tubes it is inevitable that a few droplets of potassium will become detached from the main body of potassium forming the photoelectric cathode on the inside wall of the tube. These droplets, generally at the boundary line of the window or at the beginning of the insulated support of the anode, charged up positively and reached anode potential after which they became inactive as photoelectric emitters. If the current measured was large, then these islands of emission surface were quickly charged and the cell operated quite normally with no apparent trouble. If the current was small an apparent "fatigue" was observed since the islands at first contributed to the photoelectric current for a time depending on the intensity of the light. Some time was required for the islands to return to cathode potential after the light was cut off. This restored the cell to full sensitivity and the process could be repeated. These changes in photoelectric current were observed and at first attributed to a "fatigue" effect in the phosphor. The true explanation of the effect was discovered and a new phototube constructed which was entirely free from any such difficulty.

The new photoelectric cell was made by mounting a tantalum "pill box" 3.8 cm in diameter and 4.0 cm high on a single lead tungsten-to-glass seal. The box had two openings of which one was in one end and the other in the middle of the side of the cylinder. The latter served as the window to admit the light and since the opening was one centimeter square it was covered by a "grid" of fine tantalum wires spaced about 0.1 cm apart. The anode was made from a tantalum strip 0.5 cm wide and 4 cm long and was bent in the form of a springy hoop and welded to a second single lead seal. The opening in the end plate of the "pill box" was made in the center and was just large enough to permit the anode to slide in when squeezed. A rather open seal-off constriction was attached to the glass envelope so as to point directly through this hole in the end plate. The axis of the constriction made an angle of about forty degrees with the axis of the tube. The anode seal was reentrant and about ten centimeters long so as to allow plenty of room for a long external leakage path and a guard ring which also furnished the means of supporting the tube. After the tube was thoroughly baked and the tantalum box outgassed, potassium which had been carefully distilled was shot through the constriction to give a good coating of clean potassium inside the "pill box."

The phototube was carefully shielded so that no induced charges would affect the measuring system when large changes in potential were made at the main tube. The entire system was also shielded to reduce the effect of outside disturbances and to eliminate all stray light. The photoelectric currents were measured by determining the drop produced by the current over a high resistance. A series of these were used varying from  $10^8$  ohms to  $1.5 \times 10^{10}$  ohms. An FP-54 tube used with a DuBridge-Brown<sup>5</sup> circuit served as the indicator to show when the "IR" drop was exactly balanced out by a measured e.m.f. With the amplifier sensitivity used of 5 mm per millivolt, a photoelectric current of 10<sup>-13</sup> amp. could be measured with the required accuracy.

# LIGHT OUTPUT AS A FUNCTION OF CURRENT DENSITY

Although it is often assumed that the light output from a phosphor is directly proportional to the current density when the area covered and the bombarding electron energy are constant, the

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<sup>&</sup>lt;sup>5</sup> L. A. DuBridge and H. Brown, R. S. I. 4, 532 (1933).

work of Levy and West<sup>6</sup> as well as the present study shows that there is a definite saturation effect as the current density is increased. The published data of Levy and West cover a wide variety of phosphors but show results for only one voltage and also there is some question as to the accuracy of their results at low intensities since the curves, which are plotted on a linear scale, do not pass through the origin of the graph.

The data here presented suffer from the fact that they apply to only one type of phosphor, namely willemite, but on the other hand they cover a very wide range of intensity and a wide range in voltage. The results shown in Fig. 6 are typical of many curves taken on a number of different samples of willemite obtained from different sources. In order to explain the method used in plotting Figs. 6 and 7, it will be necessary to anticipate a result which will be discussed in considerable detail in the next section of this paper. Over the low voltage range for all phosphors and over the entire observable range for some phosphors, the following empirical equation has been found<sup>7</sup> to represent the observed data with accuracy.

$$L = Q(i) \cdot (V_{sc} - V_0)^2.$$
 (4)

Here L is the light intensity,  $V_{sc}$  is the screen to cathode potential,  $V_0$  is a constant which might very well be called the "dead voltage," and Q(i) is a function of the *current density* which, according to these experiments, is the same for all samples of willemite tested. For the particular sample from which the data shown in Figs. 6 and 7 were obtained, the "dead voltage" Vo was found to be zero and therefore a plot of  $(L/V_{sc}^2)$  as a function of the current density (i) gives a graphical representation of the function Q(i) as shown in Fig. 7. The method of plotting used in Fig. 6 is in many ways more instructive since the use of "log" scales for both the abscissa and the ordinate brings out the true nature of the function in a striking manner. Over a very wide range of current density below 2.5 microamperes per sq. cm the light output was accurately directly proportional to the current density as shown by Fig. 6, since the experimental points fall along

the straight line of unit slope which may be extrapolated as far into the high current region as needed. If the observed points fall below this line a saturation effect is indicated. We may define the expression relative "efficiency" as the ratio of the observed light output at any specified current density to that read on the straight line at this same current density. With this definition we see that at 20 microamperes per sq. cm the "efficiency" has dropped to 65 percent. Another way of stating it is that 35 percent of the light which one might expect to obtain is lost due to some saturation effect. As will be shown later in this paper the "efficiency" drops to about two percent when the current density is increased as high as ten milliamperes per sq. cm (see Fig. 14).

If Eq. (4) is written in the logarithmic form as follows.

$$\log_{10} L = \log_{10} Q(i) + \log_{10} V(V_{sc}), \qquad (5)$$

it is clear that when the voltage is held constant, plots of  $\log_{10} L$  against  $\log_{10} i$  will superpose on each other if the saturation for a given phosphor is independent of the bombarding voltage. Nearly one hundred sets of measurements have been made on nine different samples of willemite at screen voltages from 500 to 6500 volts, and in all cases the function Q(i) was the same within the experimental error. The difficulty of determining the "absolute" current density was the largest source of error and this is thought not to exceed ten or fifteen percent. Relative measurements were all accurate to within about two percent.

It is very surprising indeed that the function Q(i) should be the same for all of the samples of willemite because there certainly must have been considerable difference in the concentration of "activator" present and also a difference in the state of strain in the various cases because of differences in heat treatment used in preparation. It is hoped that a systematic study can be made of this saturation effect since it is quite likely to be of importance from the standpoint of a more complete understanding of the atomic processes involved and also from the practical point of view since an increase in luminous output of ten or twenty to one at the very high current densities is not too much to hope for if this saturation loss can be greatly reduced.

Although there are important advantages in

<sup>&</sup>lt;sup>6</sup> L. Levy and D. W. West, J. I. E. E. **79**, 11 (1936). <sup>7</sup> W. B. Nottingham, Phys. Rev. **51**, 591 (1937) and Phys. Rev. **51**, 1008 (1937).



FIG. 8. Light output as a function of the bombarding energy in volts. Moderately fine grain zinc orthosilicate.

the use of the photoelectric cell for accurate measurements of light intensity, there are also certain limitations in its use. In the first place it is generally necessary to use one of the standard visual methods of measurement in order to convert the photoelectric current values into luminosity units. This can be done under conditions most favorable for accurate measurements with the illuminometer which one chooses to use and then the photoelectric cell can be utilized to make rapid and accurate relative measurements over a very wide range in intensity. In general it is very necessary that there be no change in the spectral quality of the light. This is especially important when the range of wavelengths used falls in a part of the spectrum over which the sensitivity of the cell changes very rapidly with wave-length as is the case when a potassium photoelectric cell is used to measure the green light emitted by willemite under electron bombardment. It is generally assumed that the true spectral distribution found in the light emitted is independent of the electron energy and

current density and no evidence was found in these studies to indicate the contrary. In case this work is extended an attempt will be made to test this point since the results depend very definitely on the truth of this assumption.

# LIGHT OUTPUT AS A FUNCTION OF ELECTRON ENERGY

The Lenard<sup>8</sup> law for the variation of luminosity with electron energy is

$$L = (1/C) \cdot Q \cdot (v - v_0), \qquad (6)$$

where C is a constant, Q the "beam" intensity, v the electron energy and  $v_0$  the "dead" voltage. This law has been used extensively as a practical empirical equation as for example by Leverenz<sup>9</sup> and does serve to represent a limited range of some observed data especially when the anode potential is used as a measure of the electron energy instead of the true screen potential. The work of Levy and West<sup>6</sup> shows that the candlepower increases more rapidly than the first power of the voltage although they do not make a detailed analysis of their data. An investigation by Brown<sup>10</sup> led him to conclude that for the electron energy range up to about 800 volts, the brightness B is given by the formula  $B = KJV^2$ where K is a constant. J the current density, and V the anode potential. This formula is a special case of that given in Eq. (4) which was arrived at quite independently.

The procedure found most convenient in these studies involved the observation of the luminosity as a function of the current while the potentials of all electrodes were maintained constant. For a given sample this was done at quite a number of voltages on the second anode generally between 500 volts and 8000 volts. The voltage on the first anode relative to the second was adjusted so as to bear a constant ratio to the voltage  $V_{ac}$  of either 0.2 or 0.02. This was necessary in order to keep the electron trajectories the same at all voltages. An individual set of points shown in Fig. 6, will serve to illustrate the kind of experimental data obtained although the photoelectric current was plotted as a function of the current to the second anode instead

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 <sup>&</sup>lt;sup>8</sup> P. Lenard, Ann. d. Physik, **12**, 449 (1903).
<sup>9</sup> H. W. Leverenz, J. O. S. A. **27**, 25 (1937).
<sup>10</sup> T. B. Brown, J. O. S. A. **27**, 186 (1937).

of using the photocurrent divided by the square of the screen potential as in Fig. 6. For each voltage studied, the light intensity per unit anode current was obtained by reading off the value of photoelectric current found on the straight line of unit slope on each plot at a specified value of anode current such as one microampere. The table of values thus prepared served as the basis of plots similar to those of Figs. 8 and 9. The results presented in Fig. 8 are for an RCA zinc orthosilicate with an average grain size thought to be about  $2 \times 10^{-4}$  cm in diameter supported on glass without binder. The range in voltage used on the second anode for this set of data was from 600 volts to 8000 volts. With an anode voltage of 8000 volts the screen potential was observed to be 1550 volts negative with respect to the second anode. This large difference in potential between the screen and the anode caused a reduction in the proportion of the primary beam which arrived at the test surface. Early in this investigation, it was recognized that a correction of this kind would have to be made whenever large differences in potential developed between the screen and the anode and for this reason a tube was constructed with a carefully built Faraday cage located in the aperture usually occupied by the phosphor test plate. In spite of the care used in the design of the cage secondary emission from the cage made it impossible to measure the



FIG. 9. Light output as a function of bombarding energy in volts. Very fine grain zinc orthosilicate.

spreading effect on the primary beam brought about by the difference in potential between the cage and the second anode when high voltages were used. As the second anode voltage was reduced to less than fifty volts curves taken were found to approach a limiting curve which was independent of the actual voltage but depended only on the voltage ratios used. Two curves taken at twenty and thirty volts were identical. Corrections thus arrived at and used in connection with the data in Figs. 8 and 9 are tabulated in Table I.

613	Contraction and the second second	1.197
	A DT TC	
	ABLE	1.1

FRACTION OF PRIMARY BEAM STRIKING SCREE	a SN $V_{sa}/V_{ac}$	
1.0	0	-
0.9	0.1	
0.83	0.2	
0.77	0.3	
0.71	0.4	
0.65	0.5	

Later an attempt was made to test this correction curve by depositing a very thin layer of phosphor on a conducting plate and using the variation of the light emitted as a measure of the spreading of the electron beam when the screen to cathode voltage was constant and the second anode voltage varied. The test was not satisfactory because of the poor alignment of the filament. Unfortunately it was not possible to repeat this experiment although it would no doubt give more reliable results than the Faraday cage method used.

The straight line through the points of Fig. 8 is drawn with a slope of *two* with no correction for "dead" voltage. The fact that such a correction is logical and is related to the average surface condition of the grains of the phosphor was illustrated by experiments with a coarse grain phosphor which was held to the test plate by a considerable amount of potassium silicate put on to find out what effect it might have. In this case the "dead" voltage turned out to be 450 volts. This was found in two ways. First the light intensity per unit beam current was plotted as the ordinate on log-log paper and the screen potential was plotted along the abscissa. The curve thus produced had a slope of the order of



FIG. 10. Diagram of circuit used with RCA C-730 tube investigation.

three or four at the lower end and approached a slope of two at the upper end. "Dead" voltage corrections of 400, 450, and 500 volts were tried and it was found that the 450 volt correction gave the best straight line and at the same time the slope of the line was very nearly two. If one had a good reason to believe that Eq. (4) had the correct form theoretically, then the best way of finding a good value of the constant  $V_0$  would be to plot the square root of the light per unit beam current as a function of the screen potential and determine the intercept on the voltage axis. This method was also used in this case and  $V_0$  was found to be 450 volts as expected. The fact that the constant  $V_0$  respresents an average property of the phosphor was brought out by studies of this surface which had such a high "dead" voltage. Although the light output for voltages below 450 volts was so weak that it could not be measured with the photoelectric system used, it was observable by eye down to about 300 volts.

The results shown in Fig. 9 are for a very fine grain phosphor. The average grain size was thought to be about  $3 \times 10^{-5}$  cm in diameter. Such small particles are difficult to measure and

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it is possible that some of the grains were four or five times smaller than this and some were certainly three times larger. This phosphor was deposited by the "drop" method from a milk-like suspension of the material. The analysis again showed that the light intensity increased with the square of the screen potential for voltages below 3000 volts but for voltages above this the light output increased as the 1.41 power of the electron energy expressed in volts. It is interesting to note that the penetrating power of threethousand-volt electrons is  $2.25 \times 10^{-5}$  cm for Zn<sub>2</sub>SiO<sub>4</sub> according to the calculations of Leverenz.9 On the basis of the small evidence so far obtained it is not possible to draw conclusions with certainty but one can see that the indications are that the light output from a phosphor increases as the square of the bombarding voltage unless the surface layer of the phosphor grains is disturbed in the grinding process or is covered with some impurity such as a silicate binder. This rule seems to hold for all phosphors studied up to the highest voltages obtainable depending on the secondary emission properties of the grain, if the bombarding energy is not sufficient to penetrate completely the individual grains of the phosphor.

# Screen Potentials and Luminosity Measurements as Found by Using an Experimental Nine-Inch Cathode-Ray Tube<sup>11</sup>

The C-730 tube has an electron gun with an indirectly heated cathode, a control grid, an inner anode maintained at a constant potential, and an outer anode known as the "first anode" of the tube. A conducting coating on the inside of the tube is known as the "second anode." The focusing of the electron beam depends almost

<sup>&</sup>lt;sup>11</sup> The results discussed in this section were obtained by using an experimental model of a nine-inch cathode-ray tube with the numerical designation C-730 which the Research and Engineering Department of the Radiotron Division of RCA Manufacturing Company very kindly loaned me for the time required for these tests. The results should not be taken as in any way representative of expected performance of this type of tube but must be understood to apply to this particular tube. The reason for publishing this information as it stands is that it brings out the relationship existing between many of the fundamental properties of phosphors disclosed by the investigations reported above and the performance of a phosphor in a tube of a practical design.

entirely on the ratio of the first and second anode potentials, and the intensity of the beam is governed by the potential of the control grid. Preliminary experiments using magnetic deflections and also tests of the current characteristics as observed at each collector in the tube, seemed to indicate that its performance was remarkably free from any disturbing influence of either unwanted secondary emission or gas effects. Dr. Herbert Nelson<sup>12</sup> of the Radiotron Division of the RCA Manufacturing Company, has experimented with the problem of determining the screen potential in a tube of this kind by painting a disk of "aquadag" on the outside surface of the glass and then while the glass was heated to a temperature of two or three hundred degrees centigrade by means of a hot air blast he found the potential relative to the second anode at which the disk had to be maintained so that no current flowed through the glass from the phosphor to the disk.

A diagram of the circuit used for the study of the screen potential as a function of current density and second anode voltage is shown in Fig. 10. A Compton electrometer was used to measure the currents received by the "aquadag" contact on the outside of the tube. Three contacts were made near the center of the screen area of the tube. The innermost one was a circle 0.6 cm in diameter filled in solid with "aquadag" and around this were alternate rings of nonpainted and painted surface each one of which was 0.5 cm wide. This system of two conducting rings and a center formed a target like arrangement of contacts and by means of a weak bar magnet the electron beam was deflected so as to strike near the center of the "bullseye" when the beam was focused.

With a constant bombarding voltage of 2000 volts and a beam current of  $120 \times 10^{-6}$  amp the electrometer current was measured as a function of the voltage and the slope of the curve showed the effective resistance of the Nelson "heat-contact" to be 7500 megohms when a moderate blast of hot air was used. This could be reduced to 1000 megohms by increasing the temperature of the blast. Since the electrometer was suf-

ficiently sensitive so that the lower temperature blast was perfectly satisfactory, this was used for all of the measurements to be described below.

The measurements made with the second anode voltage at 8000 volts were in some ways the most striking and are therefore shown in Fig. 11. With 1000 volts on the first anode the diameter of the beam at the screen was about 1.7 cm and the difference in potential between the "aquadag" and the second anode was only 55 volts with  $270 \times 10^{-6}$  amp. beam current. (See curve A.) With a beam current of  $160 \times 10^{-6}$ amp. the difference in potential was 44 volts. The current densities for these two cases compute out to be  $120 \times 10^{-6}$  and  $70 \times 10^{-6}$  amp. per sq. cm. As the potential on the first anode was increased, the electron beam came to a focus and then diverged again. At the focal point, the current densities for curves A and B of Fig. 11 were about  $5 \times 10^{-3}$  and  $3 \times 10^{-3}$  amp. per sq. cm, respectively and the potential differences were 1350 and 690 volts. Measurements with still higher current densities gave a limiting difference in potential of 1650 volts. It seems certain from these results as well as from observations taken with a wide range of lower second anode potentials that not all of the beam current is taken away from the screen by simple secondary emission. An obvious means at hand is that of conductivity through the screen to the second anode which is in contact with the phosphor.

The resistance R of a thin sheet of conducting



FIG. 11. Variation of "screen" potential with first anode or focusing voltage. Second anode voltage constant at 8000 volts. Curve A, grid -10 volts, beam current from  $270 \times 10^{-6}$  to  $375 \times 10^{-6}$ . Curve B, grid -15 volts, beam current from  $160 \times 10^{-6}$  to  $225 \times 10^{-6}$ .

<sup>&</sup>lt;sup>12</sup> The results of Dr. Nelson's extensive investigations with the "heat contact" which he devised are to be published in the near future.



FIG. 12. Anode to screen potential as a function of current density. Curve A, 7000 volts on second anode. Curve B, 8000 volts on second anode.

material of uniform resistivity  $\rho$  which is in the form of a ring of inside radius  $r_1$  and outside radius  $r_2$  is given by the formula

$$R = (\rho/2\pi) \cdot \ln (r_2/r_1).$$
(7)

The resistivity  $\rho$  is expressed in ohms and is the resistance across a square of any size since the resistance of such a surface is assumed to be proportional to the distance between the contacts along two sides of the square and inversely proportional to the length of the sides along which contact is made. If the resistivity of the screen were assumed to be 25 megohms, then for the case described above for which the beam diameter was 1.7 cm the resistance of the screen from the periphery of the beam to the second anode would be 10 megohms. With 55 volts as the difference in potential,  $5.5 \times 10^{-6}$  amp. would flow through the screen to the anode. This would be only two percent of the beam current. If the focused beam had a radius of only 0.02 cm the resistance of the screen would rise to only 25 megohms and yet the screen potential increased to 690 volts for curve B and 1350 volts for curve A. The assumption of a resistivity as low as 25 megohms was made in order to make the calculations as favorable as possible in support of the conductivity hypothesis. These calculations seem to show that direct conductivity to the second anode cannot be responsible for the great change in screen potential with increasing current density.

Two other possibilities seem to be worth further consideration which are first an assumed nonuniformity in the secondary emission properties of the surface. In this case the "active"

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secondary emission areas would receive electrons from the less active regions by conductivity which would give rise to a considerable difference in potential from one small region to another over the surface. The experiments so far performed give no corroborating evidence in support of this hypothesis. A second possibility is that there is a space charge effect at the surface of the phosphor since the secondary electrons have relatively small initial velocities and might require a large difference in potential between the focal point and the second anode in order to accelerate these electrons away. Again this hypothesis does not quite fit the facts as illustrated in Figs. 12 and 13.

Figure 12 shows curves A and B which represent, for 7000 and for 8000 volts on the second anode, the difference in potential between the screen and the second anode as a function of the current density. Because of the difficulty of measuring the area of the spot on the screen in the very short time during which the beam was permitted to bombard the surface and also because of the nonuniformity in the distribution of current over the beam, the points serving as the basis for the curves of Fig. 12 were rather scattered and yet it is thought that these curves are nevertheless worth reporting. The curve given in Fig. 13 bears such a complete resemblance to those of Fig. 4 that one is tempted to conclude that this represents the true behavior of the phosphor when not complicated by the complex phenomena which are responsible for the great change in screen potential as the current density in the beam is decreased. This conclusion cannot be made with reasonable certainty without further investigation.

The potassium-on-tantalum photoelectric cell, described above was used to measure the light output from the C-730 tube. A region not far from the center of the screen was selected which was free from imperfections in light distribution over the area of the beam. Here a circular opening one square centimeter in area was defined by painting "aquadag" on the end of the tube. A short focal lens was used to receive the light and focus it on the window of the photoelectric cell. Between the lens and the screen a mirror was mounted on a support so that it could be swung into place directly in front of the circular opening



FIG. 13. Screen to anode potential as a function of the second anode potential for very high current densities.

painted on the glass and in this way it was possible to adjust the size of the beam to fill the opening exactly and also properly center it. The thickness of the glass was so great that it was impossible to locate the beam properly without the use of the mirror. With the voltage on the second anode constant, the light output was measured as a function of the current in the beam. The current to the second anode thus indicated the current density directly since the cross-section area was maintained constant at one sq. cm. For each different voltage the light output was plotted as a function of the current density on log-log paper. These curves were found to superpose on each other to within the accuracy of the experiments again indicating that the saturation effect found in the previous studies depended only on the current density and was independent of the bombarding electron energy. Measurements made using higher electron densities and a smaller beam diameter fit in also with the data using the standard one sq. cm spot size. All of the results are therefore combined together in Fig. 14. The solid line was drawn through the points which numbered about a hundred in all and the two dash lines were drawn so as to include all of the observations between them. Most of the points taken were for current densities less than  $5 \times 10^{-4}$  amp. and therefore the lower part of the curve can be said to be more certain than the part above  $5 \times 10^{-4}$ amp. which was determined by only six points. The data shown in Fig. 6 agree within the experimental error with the curve of Fig. 14. There is little doubt but that current densities of the order of 10-2 amp. per sq. cm will be used in practical tubes and if this experience is at all universal then such tubes will be operating at

an efficiency far below what one might reasonably hope for. Fig. 14 shows that 98 percent of the light is lost due to the saturation effect for this particular phosphor at a current density of  $10^{-2}$  amp. per sq. cm.

Figure 15 illustrates the results obtained for the variation of light output with second anode voltage.

These data were taken by observing the light output as a function of the current density at different voltages and then after plotting these data as described above, the light output per unit current density was determined by selecting a point on the straight line portion of the log-log plot. It was noticed that after the screen was severely bombarded at high voltage and high current density, the light output with a standard low voltage and low current condition was observed to decrease. For this reason a systematic study of the light output as a function of the voltage was not undertaken using the region of the screen originally selected but another was found which had not been bombarded so strongly. The current densities used on this second one square centimeter circular opening were not allowed to exceed 10<sup>-5</sup> amp. per sq. cm. The first run was made at 3000 volts on the second anode and after this ten more runs were made at lower



FIG. 14. Light output as a function of current density. Individual curves for all voltages from 500 to 9600 volts superimposed by vertical shift only.



FIG. 15. Light output per unit current density as a function of the bombarding electron energy. Circles for initial operation at voltages below 3000 volts, dots show change in light output after high voltage bombardment.

voltages down to 500 volts. These results were accurately reproducible and are represented by the circles of Fig. 15. Following this runs were made at higher voltages and then a run was made at 1700 volts. This point shown by a dot is obviously below the value expected by interpolation by about 25 percent. More low voltage data were taken and although these were again reproducible, the results obtained in the transition region between 1000 and 2000 volts showed that a permanent change had been undergone by the phosphor. The two straight lines drawn through the points of Fig. 15 have 2.0 and 1.2 for their slopes and thus confirm the previous results illustrated by Figs. 8 and 9 that for low electron energies the light output increases with the square of the bombarding voltage. The reason for the failure of this rule above about 1500 volts should be investigated further since an increase of some five- to tenfold in the light intensity could be obtained if by using a larger grain size for example the range of application of the "square law" could be extended.

A possible explanation for the change in the rate of increase of light output with voltage is that a voltage difference between the screen and the anode was developing at the higher anode voltages in spite of the fact that the measurements using the Nelson "heat contact" showed that very little difference in potential should exist for these low current densities even up to the highest voltages used. Since the screen potential measurements were made with the glass and the screen hot, it was considered worth while to observe the effect of the application of the hot air blast on the light output. With 9600 volts on the anode, an increase in temperature first caused a 25 percent *increase* in the light while a further increase in temperature reduced the light output to 10 percent below that observed at room temperature. The same effect was observed to a less marked degree at 8000 volts. These experiments thus turned out to be inconclusive because of the complex nature of the phenomena involved and again indicate the importance of pursuing the investigation further.

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