Publications, 1931 – 1940

Electrical and Luminescent Properties of Phosphors Under Electron Bombardment

Wayne B. Nottingham*

Research Laboratory, General Electric Company, Schenectady, New York

(Received September 16, 1938)

A tube using a cathode-ray type of electron gun has been used to study the properties of five phosphor samples using four different materials. These were (1) zinc-orthosilicate (2) calcium-tungstate (3) zinc-sulfide: cadmium-sulfide and (4) zinc-sulfide. The first three showed saturation effects with current density definitely greater than the last, and the first two have maximum potentials as limited by secondary emission of 6500 and 5000 volts respectively. For these, the light output per unit electron current increased with the square of the voltage, while it increased with the 2.8 power of the voltage for the zinc-sulfide. A simple power law does not hold for the zinc-sulfide: cadmium-sulfide which shows a maximum light output at 8000 volts. All of the sulfides had such good secondary emission properties that the maximum limiting potential was well above 10,000 volts.

Introduction

THE electrical and luminescent properties of willemite under electron bombardment were investigated and reported in this Journal.[1] Those results were preliminary in the sense that definite improvements in technique were suggested which would make the conclusions drawn more certain. Although at the time there was no immediate prospect of continuing the work, this has been done with the result that the present paper not only applies to willemite but a number of other phosphors as well.

The results of the earlier study may be summarized very briefly. An investigation of the screen potential showed that, under normal conditions, it remained very slightly negative with respect to the most positive anode of the tube up to a value of voltage of the order of 6500 volts. No higher potential could be obtained with the willemite samples studied, because at this voltage one secondary electron was produced for each primary arriving at the phosphor. The light output was determined as a function of the bombarding current and found to be perfectly linear and directly proportional to the current for densities less than about two microamperes per sq. cm, but for current densities of the order of ten milliamperes per sq. cm the light output per unit current was observed to be only two percent of that found for the lower intensities. This satura-

tion effect was found to be very nearly independent of the bombarding voltage but depended only on the current density. At low current densities the light output was proportional to the square of the electron energy, except when the grain size of the willemite was so small that penetration through the individual grains was possible. Willemite held in position by binder showed an increase in light intensity with voltage which was more rapid than the second power at low voltages. Under these conditions the empirical formula incorporating the concept of "dead voltage" again indicated the applicability of a formula involving the square of the screen potential.

Two difficulties were present in the previous study: (1) Secondary emission from the first anode sometimes made the determination of the true screen potential difficult and also influenced the determination of the current density. (2) The current density measurements could not be obtained directly but had to be computed after making certain allowances which could not be tested rigorously. The design of the tube to be described below permitted the elimination of these two sources of uncertainty. Also it was considered important to investigate other materials and to determine the light output as a function of the time the electron beam is applied to the phosphor. Developments have been made to permit investigation of this aspect of the problem, but the results have not been completed, and therefore the present discussion must be confined to the investigation of the light output as a func-
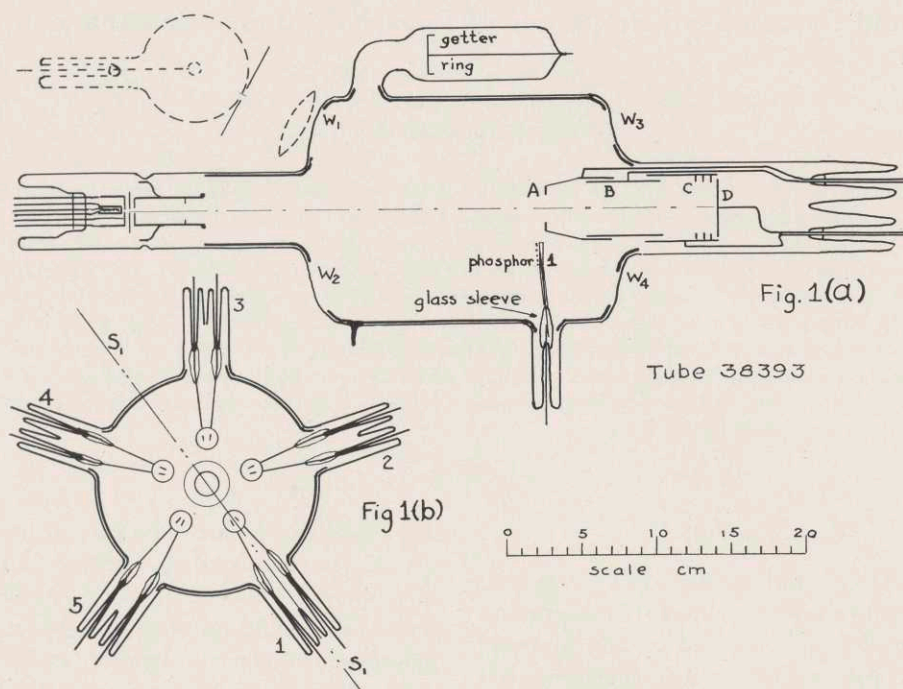
FIG. 1(a). Scale drawing of tube showing only one of the five phosphor mounts. (b) Section perpendicular to tube axis through plane of phosphor mounts.

tion of the current density and voltage with a stationary beam applied continuously to the sample.

DESIGN AND CONSTRUCTION OF THE TUBE

A standard vacuum tube blank, made of Nonex glass, designated by T-48-El, was utilized as the starting point for the experimental tube shown in Figs. 1(a) and 1(b). Although these drawings are made to scale, they are not mechanical drawings in the sense that all of the details which could be seen are given. Fig. 1(a) shows the section in the plane defined by the tube axis and the line $S_1 - S_1$ of Fig. 1(b). This shows only one of the five phosphor mounts, since an attempt to show others would only make the picture more difficult to understand. Fig. 1(b) is a section taken through the plane of the phosphor mounts perpendicular to the tube axis. The heavy line drawn as on the inside wall of the glass blank represents, in schematic, the gold coating applied to the inside wall of the tube to serve as the "second" anode and collector of the electrons. Openings about an inch in diameter are shown as

breaks in the heavy line at W_1, W_2, W_3 and W_4. There were ten of these altogether which served as windows through which the light emitted by the phosphors was measured and viewed. For example, when phosphor (1) (the only one shown in Fig. 1(a)) was being studied, a lens and photoelectric cell were located at W_1 as shown by dotted lines, and the light taken from the sample was focused on an aperture attached to the cell. This arrangement was used in order to reduce the amount of light received by the cell from phosphors not being studied, but nevertheless slightly excited by secondary electrons from the bombarded sample. The tube was mounted at the two ends on a wooden frame so arranged that the tube could be rotated about its axis. This made it unnecessary to rearrange the optical system and the photoelectric cell as different samples were investigated. All of the connecting leads to the tube were made sufficiently flexible so that it could be rotated without disconnecting any wires.

An RCA 912 cathode-ray tube gun was used as the source of electrons, and was mounted on the axis of the main tube as shown in the figure. After

having sealed the gun onto the tube, it was cracked off and remounted in an auxiliary tube for outgassing purposes. The metal parts were then heated by high frequency induction to the maximum temperature thought permissible, with the coils arranged so as not to overheat the cathode. The object in this preheating was to remove all of the easily vaporized material from the gun, so that during the final exhaust of the tube the adulteration of the surfaces of the phosphor samples would be reduced to a minimum.

A four-element electron collector was mounted on the axis of the tube directly in line with the gun, with the entrance opening practically in the same plane as the mounts supporting the phosphors being investigated. The circular opening of this electron collector was equal in diameter to that of the phosphor mounts to be described below. The object in building an electron collector as shown in the figure was to make it possible to measure the primary beam current and to determine whether or not any appreciable fraction of the beam was made up of secondary electrons from one or more of the elements of the electron gun. Furthermore, it was considered undesirable to place any of the samples on the axis of the tube, since some adulteration might come from the cathode, either by direct evaporation or as negative ion emission.

The samples were mounted on disks of 705-AO glass which were formed as shown in Fig. 1 by building up a sphere 1.5 cm in diameter on the end of two 60-mil Fernico rods which had been previously covered with a coating of this glass except for a short length used for welding. Each sphere of glass was ground and polished, leaving a disk 1.5 cm in diameter on one surface of which were exposed the two Fernico wires separated by a distance of about 4 mm. The tube blank, with its five side arms and four single lead stems used for mounting the electron collector, was connected to the vacuum system and baked for about 12 hours at 500°C. After this was done, the five side arms were cracked off and the phosphor mounts welded to the leads, with movable glass sleeves arranged so that after the welding was completed the sleeves could be put into place and melted down so as to hold them firmly. These sleeves served to eliminate the possibility that any electrons, except those which arrived there by flowing through the phosphor itself, could be collected on these leads. The conductivity of one of these mounts was measured before the application of the phosphor in a specially constructed evacuated tube, so that the resistance of the phosphor could be determined later. The conductivity, as a function of the temperature, was found to obey the equation

$$K = 130 \ e^{-11,900/T} \ (\text{ohm})^{-1}.$$

The resistance between probe wires was measured after the evacuation of the tube, and the results are tabulated in Table I. It is at once apparent that although the resistances, as shown, are low enough to make the measurement of the phosphor potential easily possible, they are many orders of magnitude higher than those previously reported.[1] The exact reason for this difference is not apparent unless it is due to the fact that the thickness of the phosphor was probably less in the present case than for the previous study of willemite. It is also possible that the acetone previously used may have left a residue which altered the conductivity.

After the construction work was finished, the five sample mounts were coated with the phosphors under investigation. These included two samples of zinc-sulfide, silver activated, which were chosen in order to get a little check on the question of reproducibility; one sample of calcium-tungstate; one of zinc-orthosilicate, manganese activated (willemite); and one of zinc-sulfide: cadmium-sulfide, silver activated. The phosphors were all ground fine enough so that they would not fall out of suspension in acetone in less than a few minutes. This size particle

TABLE I.

Sample No.	1	2	3	4	5	Glass
Phosphor	ZnS	ZnS	ZnS; CdS	2(ZnO)SiO₂	CaW	No coating
Resistance at room temperature	2.1	1.9	1.8	1.8	0.194	17×10^{14} ohms

seems to be about ideal for study, since the particle size is large enough to prohibit the complete transmission through individual grains by the electrons, and yet small enough to permit application to the mount without the use of binder. The powdered phosphors were put in acetone and, after agitation, were applied to the mounts as drops of suspended material in the liquid. By keeping the mount in motion during the time that the acetone was evaporating, it was possible to cause the phosphor to adhere to the glass plate with considerable thickness and reasonable uniformity.

Experiment showed that when the getter was mounted on the electron gun structure, as is usually done, a sufficiently thick layer of material was deposited on the phosphors to alter seriously their electrical properties. For this reason an appendix was connected to the main tube and a getter ring was mounted, as shown in the figure, using eight pellets of the King Laboratory barium-aluminum getter. During the final exhaust of the tube this ring was held at a dull red heat for a period of time sufficient to outgas it, so that when the getter was finally flashed a half an hour before sealing off the tube, very little additional gas was liberated.

After about 16 hours of baking at 480°C, the metal parts of the assembled tube were heated by high frequency until the vacuum, with these parts hot, was better than 10^{-7} mm of mercury. At this stage the cathode was activated and operated for sixteen hours with the first grid at $+9$ volts and the cathode heating current ten percent above normal. Then the seal-off constriction was preheated, and the getter flashed. After sealing off the tube the cathode was further aged by drawing a current to the first grid with a potential of ten volts applied. Tests were made to try to detect the presence of positive ions by maintaining the electron collector system, that is, parts A, B, C and D, 20 volts negative with respect to the cathode, while the electron beam was shot down the tube to the second anode with an applied potential of 5000 volts. Even with a beam current of 100 microamperes, no ion current could be detected, although the galvanometer used would have responded to a current as small as 10^{-9} ampere. The conventional method of measuring the ion current to the first grid of the electron gun also showed none that could be detected. After two months of operation the tube was again tested in this way and found to be free from detectable ion current.
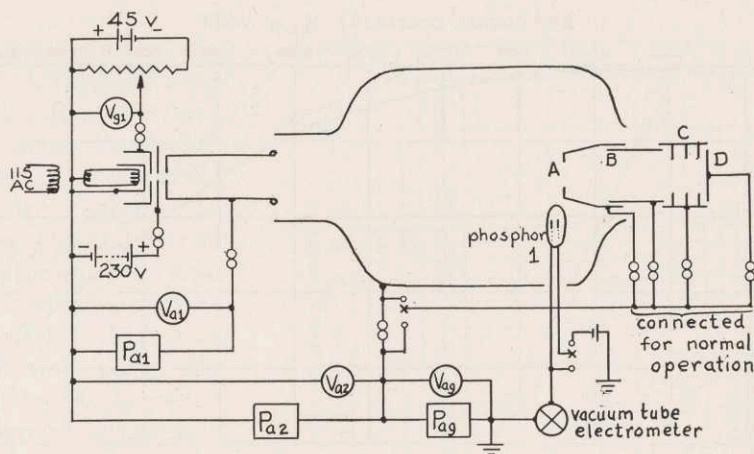
CIRCUITS

The circuit used is shown in Fig. 2, in which the three sources of d.c. power, P_{a1}, P_{a2}, P_{ag}, were very well filtered rectifier units operated from a regulated a.c. line. The voltages were read by measuring the current flowing through calibrated wire-wound resistances. The method of measurement usually involved the setting of V_{a2} (the potential on the second anode relative to the cathode) at some arbitrary value and the adjustment of V_{a1} to approximately one-tenth of this value, since for this adjustment of V_{a1} the diameter of the beam at the plane of the samples was about 1.2 cm and very nearly perfectly round and quite uniform. With this arrangement the phosphor under investigation was bombarded over nearly its entire cross section. Two permanent bar magnets served to create the magnetic field required to deflect the beam from the axis of the tube to the sample being studied. After having adjusted the potentials V_{a1} and V_{a2}, the current in the beam was controlled by varying the potential V_{g1} on the first grid. The light output was measured as a function of the current on one of a number of different photoelectric cells used in this work. Only in the case of the zinc-sulfide phosphor was there any difference in the results obtained with different photoelectric cells. A potassium photoelectric cell was used for some of the work, and found to give identical results with those obtained with a barium and a caesium cell, used with and without filters, for all phosphors except zinc-sulfide. In this case the potassium cell gave anomalous results which indicated that some slight change in the quality of the light probably took place for this phosphor.

At each value of current, the potential V_{ag} was adjusted to give zero current through the electrometer connected to the probe wire of the phosphor under investigation. This served as a direct measure of the difference in potential between the phosphor and the second anode. By subtracting V_{ag} from V_{a2}, the true potential of the phosphor relative to the cathode was determined. The results obtained are given below in

FIG. 2. Circuit diagram.

connection with the discussion of each individual phosphor studied. During these measurements all four electrodes of the electron collector were connected to the gold coating which served as the second anode, and the current measured at this electrode served as a direct measure of the primary beam current. The fact that the beam current could be measured in this direct way was proved by adjusting the magnetic field so that the beam, instead of striking either the gold coating wall or one of the phosphors, went directly through the opening of the electron collector at A of Figs. 1 and 2. In this case the current collected on the second anode proper fell to one percent of the value observed when the beam impinged either on one of the phosphors or on the wall of the tube. When the electron beam was being measured, the first electrode (A) was maintained at the second anode potential. The second one (B) was maintained 100 to 300 volts negative with respect to (A), while (C) and (D) were kept positive with respect to (A). All electrons, except for a very small fraction, were collected on (C) and (D). There was a very small current flow in the (B) circuit, indicating the escape of a small electron current, and the current measured at (A) showed that a small number of electrons were received there. This number happened to be almost exactly equal to the electrons leaving (B). In all cases these two currents were of the order of one or two percent of the primary beam current. These measurements were taken to indicate that an error of not more than two or three percent would be introduced by assuming that

the measured second anode current was equal to the primary beam current bombarding the sample.

In order to measure the currents in any part of the circuit, disregarding the potential of that part of the circuit relative to the ground, a galvanometer was set up on a single wire suspension to eliminate building vibrations[2] and enclosed completely in a conducting shield. The connecting wires and also the Ayrton shunt were enclosed in shielding. All of these shields were connected to the "battery side" of the galvanometer, so that the instrument and its surroundings were always at the same potential. This method of mounting made it possible to insert the galvanometer into any part of the circuit and have a negligible background current caused by corona discharge and other leakages. The galvanometer was connected to a plug on an insulated handle and every lead connecting to the tube had series jacks and a shunt switch (shown by the two small circles in each lead of Fig. 2), so that the galvanometer could be plugged into any lead and with the shunt open was available for reading the current.

A vacuum-tube electrometer was used to measure the small photoelectric current produced. Since in certain cases currents as small as 10^{-13} ampere were measured, polarization currents would have been objectionable were not all of the high voltage leads enclosed within a shield, and the photoelectric cell and its connections shielded

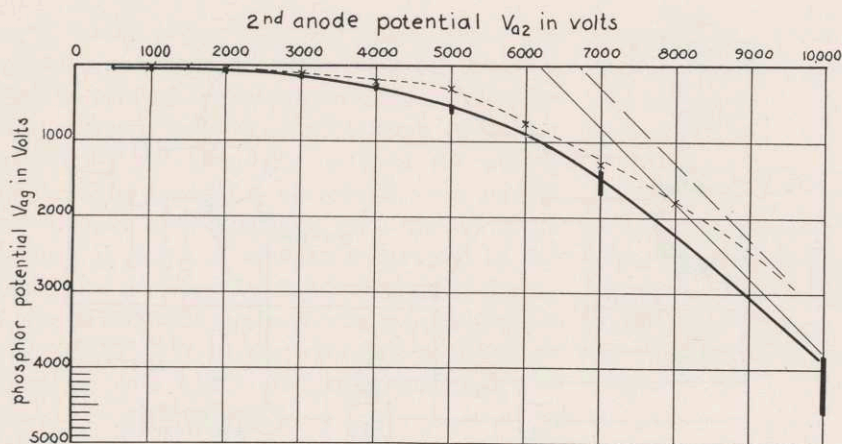[2] R. P. Johnson and W. B. Nottingham, Rev. Sci. Inst. 5, 191 (1934).

FIG. 3. Anode to phosphor potential as a function of the second anode potential. Solid line present data; dotted line previous data taken from reference 1. Heavy vertical lines show range of potential change with current density.

as well as possible. This precaution of using double shielding was necessary since neither of these two circuits could be shielded alone with the required degree of perfection to eliminate polarization currents completely. The system as a whole was also shielded to eliminate stray light and external electrical disturbances. The amplifiers used for these measurements were constructed to operate within a vacuum housing and used the DuBridge-Brown[3] circuit with FP-54 vacuum tubes.

EXPERIMENTAL RESULTS

Properties of willemite

Measurements made, according to the methods described above, on the sample of willemite showed that the screen potential remained slightly negative with respect to the second anode over the entire range of voltage from 500 to 5000. For applied potentials above 5000 the difference in potential between the screen and the second anode increased very rapidly, indicating that the maximum potential obtainable for this sample of willemite was about 6200 volts. These data are shown in Fig. 3, along with the curve (dotted) observed in the previous investigation.[1] The fact that the agreement in these two cases is so close, is a strong indication that the results are significant. If the secondary emission properties of a given phosphor sample are perfectly uniform, the observed potential

difference between the sample and the second anode should be independent of the current density. Below 5000 volts a change in observed potential of only a few volts was found with a change in current density of over a thousand-fold, while with 10,000 volts applied, the difference in potential between the sample and the anode changed from 3800 to 4600 volts as the current density was increased to about 100 microamperes per sq. cm. In all cases the difference in potential increased with increasing current density, and the extent of this change is shown by the vertical lines of Fig. 3. Although the detailed explanation of this effect is not understood, it seems reasonable to attribute it to nonuniformities of the secondary emission properties, caused either by surface contamination or a difference in the emission of certain grain facets as compared with others, depending on the crystallographic orientation of the various exposed surface planes. All of the phosphors exhibited this effect to a certain extent, although it was most prominent in the case of willemite.

In Fig. 4 typical data are shown giving the light output as a function of the current with 7000 volts applied. The heavy line of the figure which agrees very well with the present observed data shown by circles, is a reproduction of the curve taken from my earlier publication.[1] The fact that some of the points observed at current densities above 80 microamperes per sq. cm fall below the curve may be due to the heating of the sample under electron bombardment, since the beam was allowed to bombard the sample con-

[3] L. A. DuBridge and H. Brown, Rev. Sci. Inst. **4**, 532 (1933).

tinuously during the time required to take the last seven points. In spite of this objection to the experimental technique, these data have been used since they extend to somewhat higher current densities than the other data taken. Curves just like this in form were obtained at other applied voltages between 500 and 10,000 volts. The light output, as read from each curve at one microampere per sq. cm, has been plotted as a function of the voltage in Fig. 5. It is clear from inspection that the light is quite accurately proportional to the square of the energy of the bombarding electrons. A comparison of these new data with those of the earlier publication indicates a quantitative agreement throughout, in spite of the fact that the tube structures used in these two cases were entirely different, and that the sample of willemite was obtained from the same source (RCA Manufacturing Company, Harrison) with a year intervening.

Properties of calcium-tungstate

The sample of calcium-tungstate was studied over the range of 500 to 5000 volts. Curve *A* of Fig. 6 shows the results of the determination of the phosphor potential relative to the second anode. Although the data are not sufficiently complete to make possible the drawing of the limiting line with certainty, the one shown

FIG. 5. Light output as a function of the phosphor potential for the willemite sample. Straight line drawn with a slope of two.

FIG. 4. Light output as a function of the current density for the willemite sample. Second anode potential 7000 volts, phosphor potential 5500 volts. Heavy line represents results of previous study. (Reference 1).
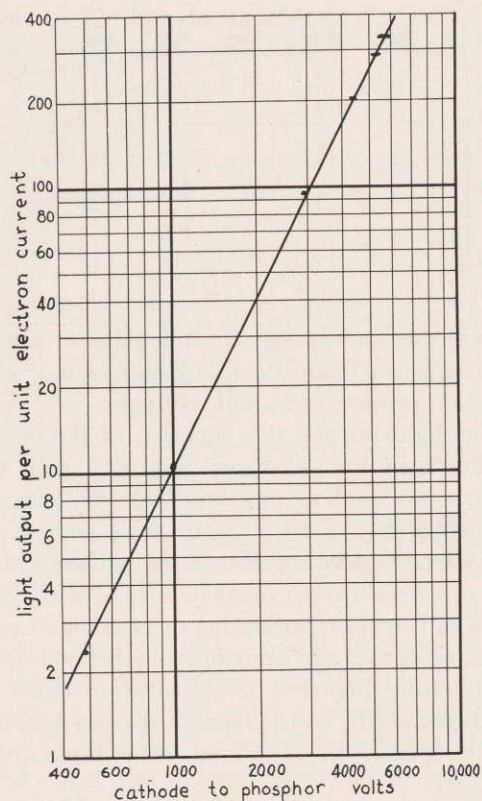
terminating at 5000 volts cannot be far off. After about two months additional operation of the tube, Dr. R. B. Nelson made a redetermination of this curve and obtained the one shown as *B* of Fig. 6. There can be no question but that the limiting line has shifted to about 7500 volts, which indicates that in spite of all of the precautions which were taken to reduce the surface contamination to a minimum, the secondary emission from the calcium-tungstate altered very definitely in the favorable direction as judged from the practical point of view. There were two possible sources of contamination which were either the cathode or the zinc-sulfide sample number 1 which was adjacent to the calcium-tungstate number 5. Although it is not certain, it seems that the latter was the more likely source, since in the course of the experiments it was severely bombarded and may have evaporated over to the calcium-tungstate sample enough to modify its secondary emission since,
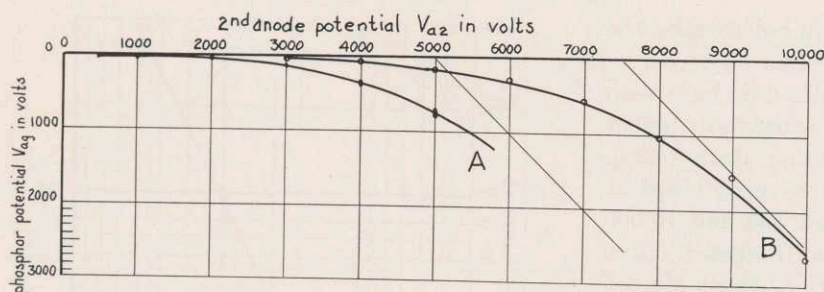
FIG. 6. Anode to phosphor potential as a function of the second anode potential. Curve A for calcium-tungstate before extended use of the tube; curve B after sufficient tube use to cause some contamination of surface.

as will be shown below, the sulfides studied were superior from the standpoint of secondary emission properties at high voltages.

The light output as a function of the current is shown in Fig. 7. From this it is seen that there was a small saturation effect which became noticeable above 20 microamperes per sq. cm. The dashed curve represents the willemite data, and has been drawn in to facilitate ready comparison. Curves representing data taken at other voltages were of the same form as the one shown, again indicating that the saturation effect depends primarily on the current density and only very slightly, if at all, on the bombarding voltage.

The circles of Fig. 8 show the light output per unit electron current as observed. These do not fall on a straight line, but, if a "dead voltage" of 100 volts is assumed and subtracted from each of the "cathode to phosphor" voltage readings, then a straight line, with a slope of two, results as indicated by the crosses.

Properties of zinc-sulfide: cadmium-sulfide; silver activated

The sample of zinc-sulfide : cadmium-sulfide was investigated over the same current and voltage range as described above. In view of the fact that so very little seems to be known about the secondary emission properties of the sulfides, it was very interesting to observe that the potential difference between this sample and the second anode remained small, even with 10,000 volts applied. In fact, here the difference in potential was found to be about 100 volts, depending slightly on the current density and location of the beam on the sample when focused. As will be mentioned below, the two samples of zinc-sulfide also showed this favorable property of giving good secondary emission up to 10,000

volts. It would be interesting and important to determine the maximum potential which could be used with the sulfides, but with the apparatus and time available, it was not possible to carry on these tests. The light output as a function of the current was accurately linear for current densities less than one microampere per sq. cm. Above this the light output per unit current decreased to almost exactly the same extent as was found for willemite. The dashed line of Fig. 9 represents the willemite data. As is shown, there was a drop in output of about 50 percent at about 100 microamperes per sq. cm, which was practically independent of the anode voltage. Another very unexpected effect is illustrated in Fig. 10, in which the light output is shown as a function of the voltage. At very low voltages, the light increased with the square of the voltage, but, as the curve shows, this rate of increase did not continue. In fact, above 4000 volts the in-
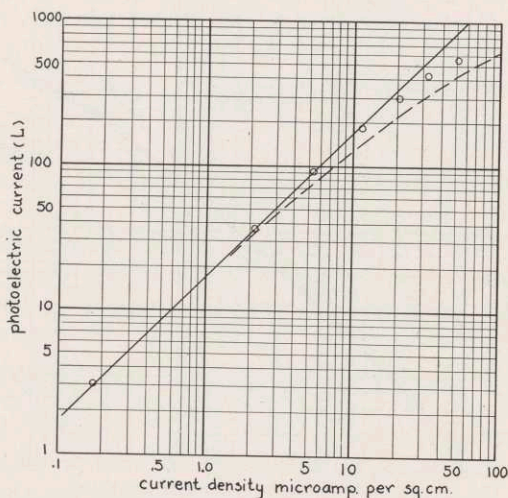
FIG. 7. Light output as a function of current density for the calcium-tungstate sample taken at 5000 volts applied. Phosphor potential 4300 volts to cathode. Dashed line willemite curve for comparison.

80

crease is even less than the first power.* This type of curve is particularly interesting in that it shows that if one were to use the rate of increase of light intensity with voltage as an indirect measure of the potential of the phosphor, the deductions on this basis would be decidedly in error, since direct measurements indicated that the potential of the phosphor throughout the entire observable range differed very little from that of the anode, and yet the rate at which the light output increased with voltage might be taken mistakenly as an indication that the potential of the phosphor had remained fixed at some relatively low voltage.

FIG. 8. Circles show light output per unit electron current as a function of the phosphor potential for calcium-tungstate. Crosses assuming a "dead voltage" of 100 volts. Straight line drawn with slope of two.

Properties of zinc-sulfide; silver activated

Silver activated zinc-sulfide was deposited on two of the test plates. These two samples were

* Dr. F. Seitz has suggested that this effect may be due to the excitation of x-ray levels in the cadmium atoms, with the resultant loss in electron energy, and therefore a decrease in the light-producing efficiency with increased voltage.
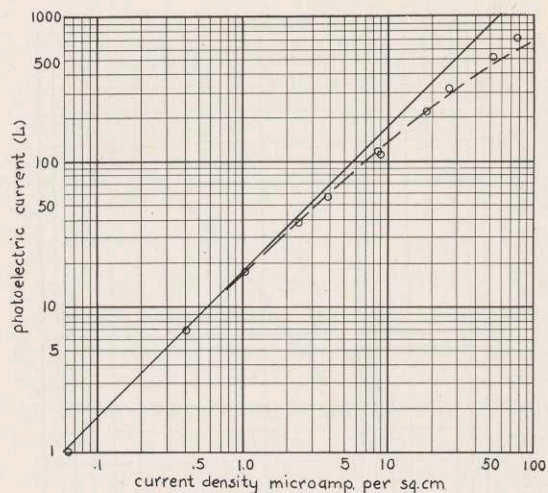
FIG. 9. Light output as a function of current density for the zinc-sulfide: cadmium-sulfide sample taken with 5000 volts applied. Phosphor potential 4970 volts. Dashed line is willemite curve for comparison.

similar in their behavior in all respects, and again showed that sulfides are good secondary emitters up to 10,000 volts and are probably able to go to much higher voltages than this. Another important property of these two samples of zinc-sulfide was that the light output per unit area was directly proportional to the current density to much higher values than for any other phosphor examined in this study. There was no detectable saturation effect up to 100 microamperes per sq. cm. At 3000 volts and with a sharply focused beam giving a current density of about ten milliamperes per sq. cm, the light output dropped to 40 percent of that expected on the assumption of perfect linearity between light output per unit area and current density. With this current density, willemite delivered only two percent of the expected light. Very extensive data were taken on these two phosphors because it was noticed that nearly all curves plotted showing the logarithm of the light output as a function of the logarithm of the current were good straight lines with a slope slightly in excess of unity. Some data showed an excess of as much as five or six percent. Since this was most noticeable with the lower anode voltages, where on account of the weakness of the light the errors are greatest, it must be assumed for the present that this apparent increase in light output above that expected was too near the limit set
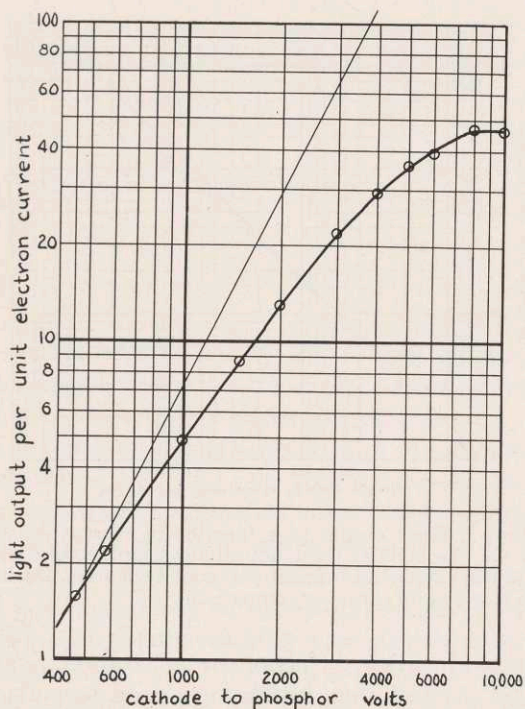
FIG. 10. Light output as a function of the electron energy for the zinc-sulfide: cadmium-sulfide sample. Straight line drawn with a slope of two.

by errors of measurement to be established without additional experiments.

Figure 11 shows the logarithm of the light output at constant current as a function of the logarithm of the electron energy in volts. The results obtained on both samples are shown, and, as is indicated, the slope observed on sample No. 1 was 2.8 while that for No. 2 was 2.9. These results were indeed surprising and can be taken as an indication that there must be some fundamental difference in the excitation process for zinc-sulfide as compared with willemite and calcium-tungstate. As long as the actual efficiency of the process in terms of watts input and light energy output is small, an increase in light output with the square of the voltage can be interpreted as showing that the number of excited centers produced per unit path length of the primary electron is independent of the electron energy, and therefore the light output is proportional to the penetration which, according to Leverenz,[4] is proportional to the square of the electron energy. A light output increasing more rapidly

[4] H. W. Leverenz, J. Opt. Soc. Am. **27**, 25 (1937).

82

than the square of the voltage may perhaps be an indication that excited centers are produced more efficiently by a high energy electron for each unit of path length.

SUMMARY OF RESULTS

As a result of these studies, the following conclusions seem to be justified.

(1) For low current densities the light output per unit area is accurately proportional to the current density. This is the equivalent of stating that for low current densities the light per unit of current is *constant*.

(2) With increased current density the light per unit current at constant voltage falls by an amount which depends primarily on the current density. The function representing this relation is nearly independent of the bombarding voltage. The slight dependence seems to be in the direc-
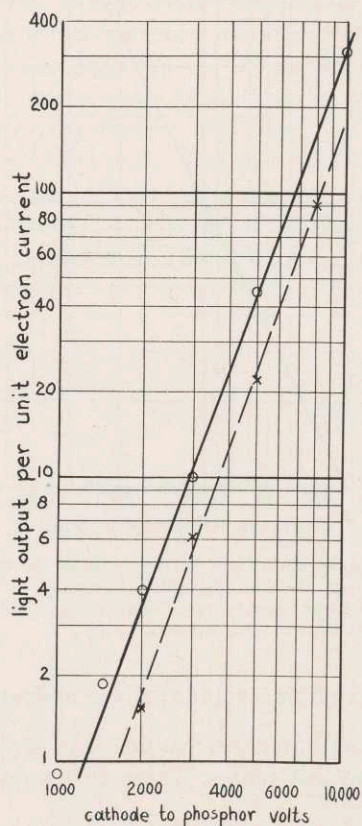

FIG. 11. Light output as a function of the electron energy for two samples of zinc-sulfide. Solid line for No. 1 and dashed line for No. 2. Straight lines drawn with slopes of 2.8 and 2.9. (The vertical separation is not significant.)

tion of a smaller saturation effect as the voltage is increased. A twenty percent loss in light per unit current was observed at the current densities given in Table II for the various phosphors.

(3) Except for the zinc-sulfide : cadmium-sulfide phosphor, the light per unit current at low densities, as a function of the electron energy V, was well represented by the empirical equation $(L/i) = A(V-V_0)^n$, where L/i is the light per unit current, A a constant, V_0 the so-called "dead voltage," generally zero, and n an exponent characteristic of the phosphor, tabulated in column three of Table II.

(4) Secondary emission properties of insulated phosphors operated in high vacuum determine the maximum useful operating voltage as discussed at length in the previous paper.[1] For conditions which are thought to correspond to the uncontaminated state of the materials, the upper limits of potential are given in column four of Table II.

For the opportunity to carry through the experiments upon which this paper is based, I am

TABLE II.

PHOSPHOR		MICROAMP. PER SQ. CM FOR 20% LOSS IN LIGHT	"n," POWER OF VOLTAGE FACTOR	MAXIMUM LIMITING VOLTAGE
CRYSTAL	ACTIVATOR			
$2(ZnO)SiO_2$	Mn	10	2	6500
ZnS; CdS	Ag	10	variable	>10,000
$CaWO_4$		30	2	5000
ZnS	Ag	200	2.8	>10,000

ELECTRICAL AND LUMINESCENT PROPERTIES OF
PHOSPHORS UNDER ELECTRON BOMBARDMENT

By
WAYNE B. NOTTINGHAM

Electrical and Luminescent Properties of Phosphors Under Electron Bombardment

WAYNE B. NOTTINGHAM*
Research Laboratory, General Electric Company, Schenectady, New York

A tube using a cathode-ray type of electron gun has been used to study the properties of five phosphor samples using four different materials. These were (1) zinc-orthosilicate (2) calcium-tungstate (3) zinc-sulfide: cadmium-sulfide and (4) zinc-sulfide. The first three showed saturation effects with current density definitely greater than the last, and the first two have maximum potentials as limited by secondary emission of 6500 and 5000 volts respectively. For these, the light output per unit electron current increased with the square of the voltage, while it increased with the 2.8 power of the voltage for the zinc-sulfide. A simple power law does not hold for the zinc-sulfide: cadmium-sulfide which shows a maximum light output at 8000 volts. All of the sulfides had such good secondary emission properties that the maximum limiting potential was well above 10,000 volts.

INTRODUCTION

THE electrical and luminescent properties of willemite under electron bombardment were investigated and reported in this Journal.[1] Those results were preliminary in the sense that definite improvements in technique were suggested which would make the conclusions drawn more certain. Although at the time there was no immediate prospect of continuing the work, this has been done with the result that the present paper not only applies to willemite but a number of other phosphors as well.

The results of the earlier study may be summarized very briefly. An investigation of the screen potential showed that, under normal conditions, it remained very slightly negative with respect to the most positive anode of the tube up to a value of voltage of the order of 6500 volts. No higher potential could be obtained with the willemite samples studied, because at this voltage one secondary electron was produced for each primary arriving at the phosphor. The light output was determined as a function of the bombarding current and found to be perfectly linear and directly proportional to the current for densities less than about two microamperes per sq. cm, but for current densities of the order of ten milliamperes per sq. cm the light output per unit current was observed to be only two percent of that found for the lower intensities. This satura-

tion effect was found to be very nearly independent of the bombarding voltage but depended only on the current density. At low current densities the light output was proportional to the square of the electron energy, except when the grain size of the willemite was so small that penetration through the individual grains was possible. Willemite held in position by binder showed an increase in light intensity with voltage which was more rapid than the second power at low voltages. Under these conditions the empirical formula incorporating the concept of "dead voltage" again indicated the applicability of a formula involving the square of the screen potential.

Two difficulties were present in the previous study: (1) Secondary emission from the first anode sometimes made the determination of the true screen potential difficult and also influenced the determination of the current density. (2) The current density measurements could not be obtained directly but had to be computed after making certain allowances which could not be tested rigorously. The design of the tube to be described below permitted the elimination of these two sources of uncertainty. Also it was considered important to investigate other materials and to determine the light output as a function of the time the electron beam is applied to the phosphor. Developments have been made to permit investigation of this aspect of the problem, but the results have not been completed, and therefore the present discussion must be confined to the investigation of the light output as a func-
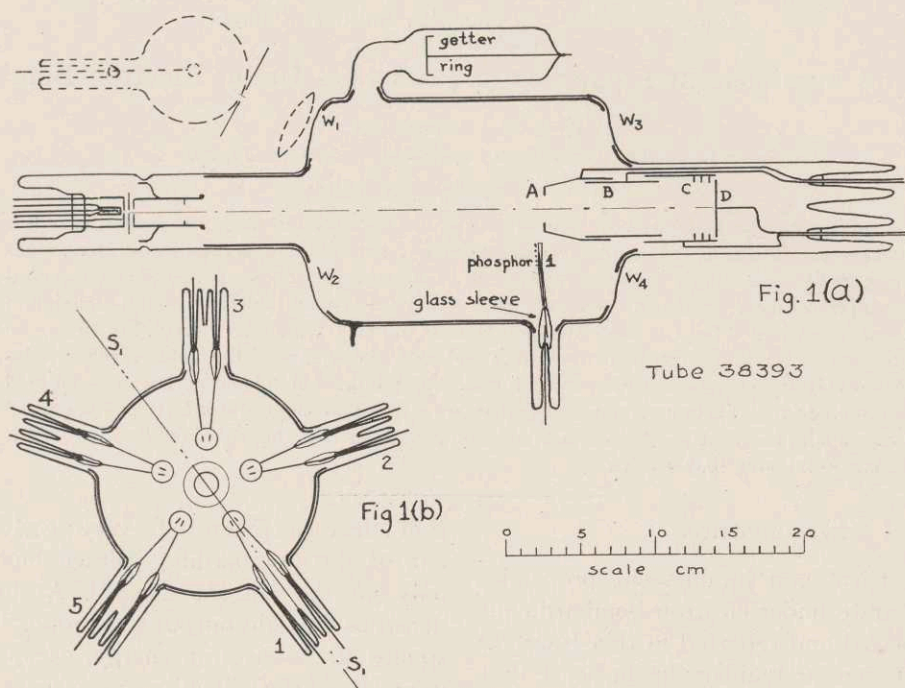

FIG. 1(a). Scale drawing of tube showing only one of the five phosphor mounts. (b) Section perpendicular to tube axis through plane of phosphor mounts.

tion of the current density and voltage with a stationary beam applied continuously to the sample.

DESIGN AND CONSTRUCTION OF THE TUBE

A standard vacuum tube blank, made of Nonex glass, designated by T-48-El, was utilized as the starting point for the experimental tube shown in Figs. 1(a) and 1(b). Although these drawings are made to scale, they are not mechanical drawings in the sense that all of the details which could be seen are given. Fig. 1(a) shows the section in the plane defined by the tube axis and the line $S_1 - S_1$ of Fig. 1(b). This shows only one of the five phosphor mounts, since an attempt to show others would only make the picture more difficult to understand. Fig. 1(b) is a section taken through the plane of the phosphor mounts perpendicular to the tube axis. The heavy line drawn as on the inside wall of the glass blank represents, in schematic, the gold coating applied to the inside wall of the tube to serve as the "second" anode and collector of the electrons. Openings about an inch in diameter are shown as

breaks in the heavy line at W_1, W_2, W_3 and W_4. There were ten of these altogether which served as windows through which the light emitted by the phosphors was measured and viewed. For example, when phosphor (1) (the only one shown in Fig. 1(a)) was being studied, a lens and photoelectric cell were located at W_1 as shown by dotted lines, and the light taken from the sample was focused on an aperture attached to the cell. This arrangement was used in order to reduce the amount of light received by the cell from phosphors not being studied, but nevertheless slightly excited by secondary electrons from the bombarded sample. The tube was mounted at the two ends on a wooden frame so arranged that the tube could be rotated about its axis. This made it unnecessary to rearrange the optical system and the photoelectric cell as different samples were investigated. All of the connecting leads to the tube were made sufficiently flexible so that it could be rotated without disconnecting any wires.

An RCA 912 cathode-ray tube gun was used as the source of electrons, and was mounted on the axis of the main tube as shown in the figure. After

having sealed the gun onto the tube, it was cracked off and remounted in an auxiliary tube for outgassing purposes. The metal parts were then heated by high frequency induction to the maximum temperature thought permissible, with the coils arranged so as not to overheat the cathode. The object in this preheating was to remove all of the easily vaporized material from the gun, so that during the final exhaust of the tube the adulteration of the surfaces of the phosphor samples would be reduced to a minimum.

A four-element electron collector was mounted on the axis of the tube directly in line with the gun, with the entrance opening practically in the same plane as the mounts supporting the phosphors being investigated. The circular opening of this electron collector was equal in diameter to that of the phosphor mounts to be described below. The object in building an electron collector as shown in the figure was to make it possible to measure the primary beam current and to determine whether or not any appreciable fraction of the beam was made up of secondary electrons from one or more of the elements of the electron gun. Furthermore, it was considered undesirable to place any of the samples on the axis of the tube, since some adulteration might come from the cathode, either by direct evaporation or as negative ion emission.

The samples were mounted on disks of 705-AO glass which were formed as shown in Fig. 1 by building up a sphere 1.5 cm in diameter on the end of two 60-mil Fernico rods which had been previously covered with a coating of this glass except for a short length used for welding. Each sphere of glass was ground and polished, leaving a disk 1.5 cm in diameter on one surface of which were exposed the two Fernico wires separated by a distance of about 4 mm. The tube blank, with its five side arms and four single lead stems used for mounting the electron collector, was connected to the vacuum system and baked for about 12 hours at 500°C. After this was done, the five

side arms were cracked off and the phosphor mounts welded to the leads, with movable glass sleeves arranged so that after the welding was completed the sleeves could be put into place and melted down so as to hold them firmly. These sleeves served to eliminate the possibility that any electrons, except those which arrived there by flowing through the phosphor itself, could be collected on these leads. The conductivity of one of these mounts was measured before the application of the phosphor in a specially constructed evacuated tube, so that the resistance of the phosphor could be determined later. The conductivity, as a function of the temperature, was found to obey the equation

$$K = 130 \, e^{-11,900/T} \, (\text{ohm})^{-1}.$$

The resistance between probe wires was measured after the evacuation of the tube, and the results are tabulated in Table I. It is at once apparent that although the resistances, as shown, are low enough to make the measurement of the phosphor potential easily possible, they are many orders of magnitude higher than those previously reported.[1] The exact reason for this difference is not apparent unless it is due to the fact that the thickness of the phosphor was probably less in the present case than for the previous study of willemite. It is also possible that the acetone previously used may have left a residue which altered the conductivity.

After the construction work was finished, the five sample mounts were coated with the phosphors under investigation. These included two samples of zinc-sulfide, silver activated, which were chosen in order to get a little check on the question of reproducibility; one sample of calcium-tungstate; one of zinc-orthosilicate, manganese activated (willemite); and one of zinc-sulfide: cadmium-sulfide, silver activated. The phosphors were all ground fine enough so that they would not fall out of suspension in acetone in less than a few minutes. This size particle

TABLE I.

Sample No.	1	2	3	4	5	Glass
Phosphor	ZnS	ZnS	ZnS; CdS	2(ZnO)SiO$_2$	CaW	No coating
Resistance at room temperature	2.1	1.9	1.8	1.8	0.194	17×10^{14} ohms

seems to be about ideal for study, since the particle size is large enough to prohibit the complete transmission through individual grains by the electrons, and yet small enough to permit application to the mount without the use of binder. The powdered phosphors were put in acetone and, after agitation, were applied to the mounts as drops of suspended material in the liquid. By keeping the mount in motion during the time that the acetone was evaporating, it was possible to cause the phosphor to adhere to the glass plate with considerable thickness and reasonable uniformity.

Experiment showed that when the getter was mounted on the electron gun structure, as is usually done, a sufficiently thick layer of material was deposited on the phosphors to alter seriously their electrical properties. For this reason an appendix was connected to the main tube and a getter ring was mounted, as shown in the figure, using eight pellets of the King Laboratory barium-aluminum getter. During the final exhaust of the tube this ring was held at a dull red heat for a period of time sufficient to outgas it, so that when the getter was finally flashed a half an hour before sealing off the tube, very little additional gas was liberated.

After about 16 hours of baking at 480°C, the metal parts of the assembled tube were heated by high frequency until the vacuum, with these parts hot, was better than 10^{-7} mm of mercury. At this stage the cathode was activated and operated for sixteen hours with the first grid at $+9$ volts and the cathode heating current ten percent above normal. Then the seal-off constriction was preheated, and the getter flashed. After sealing off the tube the cathode was further aged by drawing a current to the first grid with a potential of ten volts applied. Tests were made to try to detect the presence of positive ions by maintaining the electron collector system, that is, parts A, B, C and D, 20 volts negative with respect to the cathode, while the electron beam was shot down the tube to the second anode with an applied potential of 5000 volts. Even with a beam current of 100 microamperes, no ion current could be detected, although the galvanometer used would have responded to a current as small as 10^{-9} ampere. The conventional method of measuring the ion current to the first grid of the

electron gun also showed none that could be detected. After two months of operation the tube was again tested in this way and found to be free from detectable ion current.
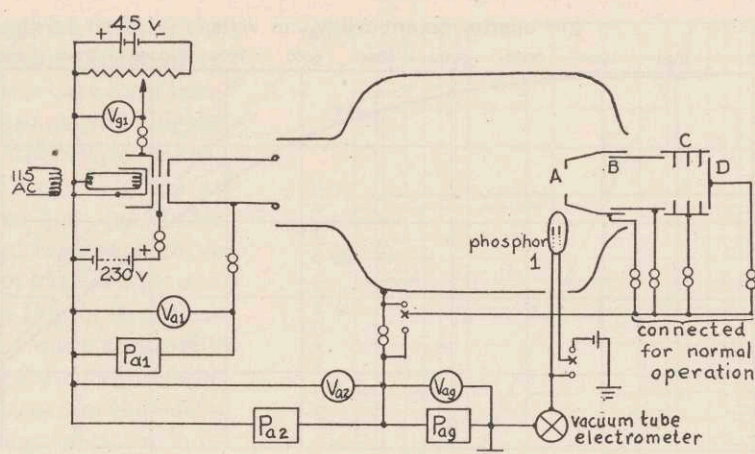
CIRCUITS

The circuit used is shown in Fig. 2, in which the three sources of d.c. power, P_{a1}, P_{a2}, P_{ag}, were very well filtered rectifier units operated from a regulated a.c. line. The voltages were read by measuring the current flowing through calibrated wire-wound resistances. The method of measurement usually involved the setting of V_{a2} (the potential on the second anode relative to the cathode) at some arbitrary value and the adjustment of V_{a1} to approximately one-tenth of this value, since for this adjustment of V_{a1} the diameter of the beam at the plane of the samples was about 1.2 cm and very nearly perfectly round and quite uniform. With this arrangement the phosphor under investigation was bombarded over nearly its entire cross section. Two permanent bar magnets served to create the magnetic field required to deflect the beam from the axis of the tube to the sample being studied. After having adjusted the potentials V_{a1} and V_{a2}, the current in the beam was controlled by varying the potential V_{g1} on the first grid. The light output was measured as a function of the current on one of a number of different photoelectric cells used in this work. Only in the case of the zinc-sulfide phosphor was there any difference in the results obtained with different photoelectric cells. A potassium photoelectric cell was used for some of the work, and found to give identical results with those obtained with a barium and a caesium cell, used with and without filters, for all phosphors except zinc-sulfide. In this case the potassium cell gave anomalous results which indicated that some slight change in the quality of the light probably took place for this phosphor.

At each value of current, the potential V_{ag} was adjusted to give zero current through the electrometer connected to the probe wire of the phosphor under investigation. This served as a direct measure of the difference in potential between the phosphor and the second anode. By subtracting V_{ag} from V_{a2}, the true potential of the phosphor relative to the cathode was determined. The results obtained are given below in

Fig. 2. Circuit diagram.

connection with the discussion of each individual phosphor studied. During these measurements all four electrodes of the electron collector were connected to the gold coating which served as the second anode, and the current measured at this electrode served as a direct measure of the primary beam current. The fact that the beam current could be measured in this direct way was proved by adjusting the magnetic field so that the beam, instead of striking either the gold coating wall or one of the phosphors, went directly through the opening of the electron collector at A of Figs. 1 and 2. In this case the current collected on the second anode proper fell to one percent of the value observed when the beam impinged either on one of the phosphors or on the wall of the tube. When the electron beam was being measured, the first electrode (A) was maintained at the second anode potential. The second one (B) was maintained 100 to 300 volts negative with respect to (A), while (C) and (D) were kept positive with respect to (A). All electrons, except for a very small fraction, were collected on (C) and (D). There was a very small current flow in the (B) circuit, indicating the escape of a small electron current, and the current measured at (A) showed that a small number of electrons were received there. This number happened to be almost exactly equal to the electrons leaving (B). In all cases these two currents were of the order of one or two percent of the primary beam current. These measurements were taken to indicate that an error of not more than two or three percent would be introduced by assuming that

the measured second anode current was equal to the primary beam current bombarding the sample.

In order to measure the currents in any part of the circuit, disregarding the potential of that part of the circuit relative to the ground, a galvanometer was set up on a single wire suspension to eliminate building vibrations[2] and enclosed completely in a conducting shield. The connecting wires and also the Ayrton shunt were enclosed in shielding. All of these shields were connected to the "battery side" of the galvanometer, so that the instrument and its surroundings were always at the same potential. This method of mounting made it possible to insert the galvanometer into any part of the circuit and have a negligible background current caused by corona discharge and other leakages. The galvanometer was connected to a plug on an insulated handle and every lead connecting to the tube had series jacks and a shunt switch (shown by the two small circles in each lead of Fig. 2), so that the galvanometer could be plugged into any lead and with the shunt open was available for reading the current.

A vacuum-tube electrometer was used to measure the small photoelectric current produced. Since in certain cases currents as small as 10^{-13} ampere were measured, polarization currents would have been objectionable were not all of the high voltage leads enclosed within a shield, and the photoelectric cell and its connections shielded

[2] R. P. Johnson and W. B. Nottingham, Rev. Sci. Inst. 5, 191 (1934).

2nd anode potential V_{a2} in volts

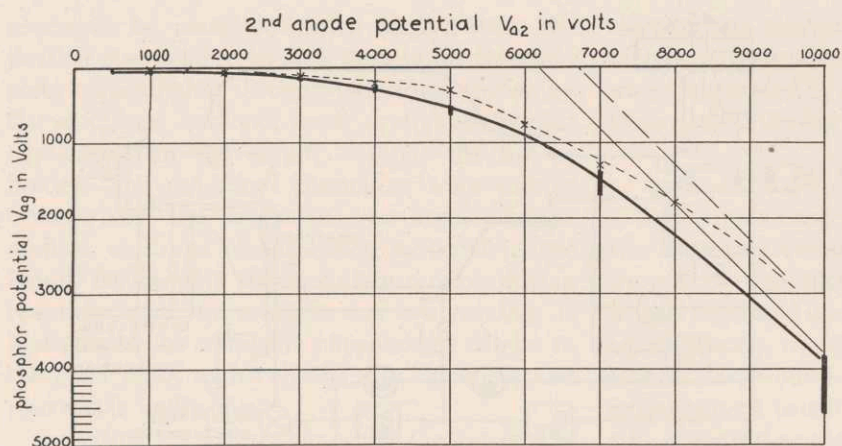phosphor potential V_{ag} in Volts

Fig. 3. Anode to phosphor potential as a function of the second anode potential. Solid line present data; dotted line previous data taken from reference 1. Heavy vertical lines show range of potential change with current density.

as well as possible. This precaution of using double shielding was necessary since neither of these two circuits could be shielded alone with the required degree of perfection to eliminate polarization currents completely. The system as a whole was also shielded to eliminate stray light and external electrical disturbances. The amplifiers used for these measurements were constructed to operate within a vacuum housing and used the DuBridge-Brown[3] circuit with FP-54 vacuum tubes.

EXPERIMENTAL RESULTS

Properties of willemite

Measurements made, according to the methods described above, on the sample of willemite showed that the screen potential remained slightly negative with respect to the second anode over the entire range of voltage from 500 to 5000. For applied potentials above 5000 the difference in potential between the screen and the second anode increased very rapidly, indicating that the maximum potential obtainable for this sample of willemite was about 6200 volts. These data are shown in Fig. 3, along with the curve (dotted) observed in the previous investigation.[1] The fact that the agreement in these two cases is so close, is a strong indication that the results are significant. If the secondary emission properties of a given phosphor sample are perfectly uniform, the observed potential

difference between the sample and the second anode should be independent of the current density. Below 5000 volts a change in observed potential of only a few volts was found with a change in current density of over a thousand-fold, while with 10,000 volts applied, the difference in potential between the sample and the anode changed from 3800 to 4600 volts as the current density was increased to about 100 microamperes per sq. cm. In all cases the difference in potential increased with increasing current density, and the extent of this change is shown by the vertical lines of Fig. 3. Although the detailed explanation of this effect is not understood, it seems reasonable to attribute it to nonuniformities of the secondary emission properties, caused either by surface contamination or a difference in the emission of certain grain facets as compared with others, depending on the crystallographic orientation of the various exposed surface planes. All of the phosphors exhibited this effect to a certain extent, although it was most prominent in the case of willemite.

In Fig. 4 typical data are shown giving the light output as a function of the current with 7000 volts applied. The heavy line of the figure which agrees very well with the present observed data shown by circles, is a reproduction of the curve taken from my earlier publication.[1] The fact that some of the points observed at current densities above 80 microamperes per sq. cm fall below the curve may be due to the heating of the sample under electron bombardment, since the beam was allowed to bombard the sample con-

[3] L. A. DuBridge and H. Brown, Rev. Sci. Inst. 4, 532 (1933).

tinuously during the time required to take the last seven points. In spite of this objection to the experimental technique, these data have been used since they extend to somewhat higher current densities than the other data taken. Curves just like this in form were obtained at other applied voltages between 500 and 10,000 volts. The light output, as read from each curve at one microampere per sq. cm, has been plotted as a function of the voltage in Fig. 5. It is clear from inspection that the light is quite accurately proportional to the square of the energy of the bombarding electrons. A comparison of these new data with those of the earlier publication indicates a quantitative agreement throughout, in spite of the fact that the tube structures used in these two cases were entirely different, and that the sample of willemite was obtained from the same source (RCA Manufacturing Company, Harrison) with a year intervening.

Properties of calcium-tungstate

The sample of calcium-tungstate was studied over the range of 500 to 5000 volts. Curve A of Fig. 6 shows the results of the determination of the phosphor potential relative to the second anode. Although the data are not sufficiently complete to make possible the drawing of the limiting line with certainty, the one shown

FIG. 5. Light output as a function of the phosphor potential for the willemite sample. Straight line drawn with a slope of two.
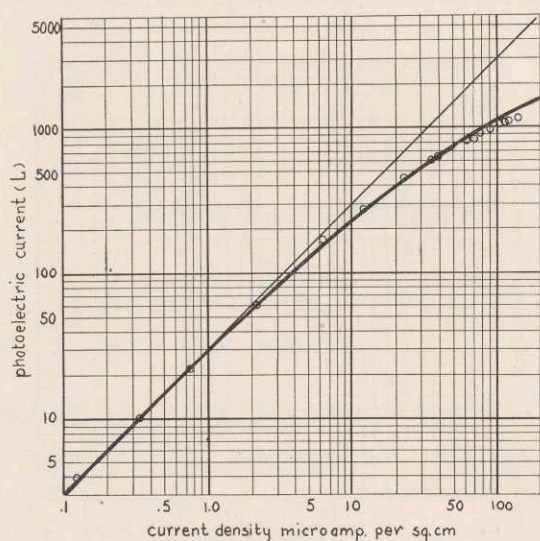
FIG. 4. Light output as a function of the current density for the willemite sample. Second anode potential 7000 volts, phosphor potential 5500 volts. Heavy line represents results of previous study. (Reference 1).
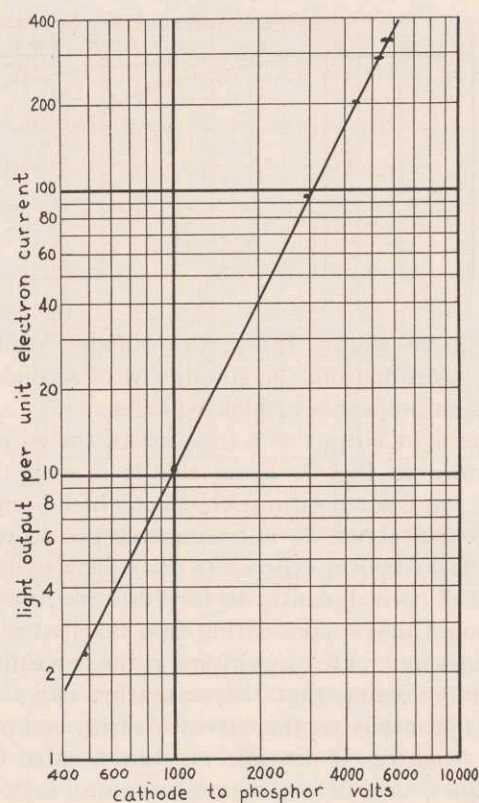
terminating at 5000 volts cannot be far off. After about two months additional operation of the tube, Dr. R. B. Nelson made a redetermination of this curve and obtained the one shown as B of Fig. 6. There can be no question but that the limiting line has shifted to about 7500 volts, which indicates that in spite of all of the precautions which were taken to reduce the surface contamination to a minimum, the secondary emission from the calcium-tungstate altered very definitely in the favorable direction as judged from the practical point of view. There were two possible sources of contamination which were either the cathode or the zinc-sulfide sample number 1 which was adjacent to the calcium-tungstate number 5. Although it is not certain, it seems that the latter was the more likely source, since in the course of the experiments it was severely bombarded and may have evaporated over to the calcium-tungstate sample enough to modify its secondary emission since,
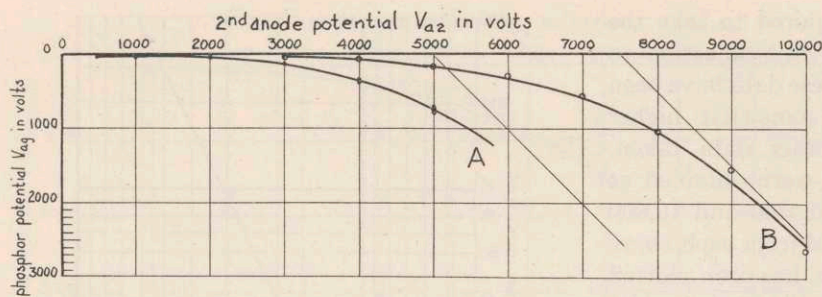
FIG. 6. Anode to phosphor potential as a function of the second anode potential. Curve A for calcium-tungstate before extended use of the tube; curve B after sufficient tube use to cause some contamination of surface.

as will be shown below, the sulfides studied were superior from the standpoint of secondary emission properties at high voltages.

The light output as a function of the current is shown in Fig. 7. From this it is seen that there was a small saturation effect which became noticeable above 20 microamperes per sq. cm. The dashed curve represents the willemite data, and has been drawn in to facilitate ready comparison. Curves representing data taken at other voltages were of the same form as the one shown, again indicating that the saturation effect depends primarily on the current density and only very slightly, if at all, on the bombarding voltage.

The circles of Fig. 8 show the light output per unit electron current as observed. These do not fall on a straight line, but, if a "dead voltage" of 100 volts is assumed and subtracted from each of the "cathode to phosphor" voltage readings, then a straight line, with a slope of two, results as indicated by the crosses.

Properties of zinc-sulfide: cadmium-sulfide; silver activated

The sample of zinc-sulfide : cadmium-sulfide was investigated over the same current and voltage range as described above. In view of the fact that so very little seems to be known about the secondary emission properties of the sulfides, it was very interesting to observe that the potential difference between this sample and the second anode remained small, even with 10,000 volts applied. In fact, here the difference in potential was found to be about 100 volts, depending slightly on the current density and location of the beam on the sample when focused. As will be mentioned below, the two samples of zinc-sulfide also showed this favorable property of giving good secondary emission up to 10,000

volts. It would be interesting and important to determine the maximum potential which could be used with the sulfides, but with the apparatus and time available, it was not possible to carry on these tests. The light output as a function of the current was accurately linear for current densities less than one microampere per sq. cm. Above this the light output per unit current decreased to almost exactly the same extent as was found for willemite. The dashed line of Fig. 9 represents the willemite data. As is shown, there was a drop in output of about 50 percent at about 100 microamperes per sq. cm, which was practically independent of the anode voltage. Another very unexpected effect is illustrated in Fig. 10, in which the light output is shown as a function of the voltage. At very low voltages, the light increased with the square of the voltage, but, as the curve shows, this rate of increase did not continue. In fact, above 4000 volts the in-
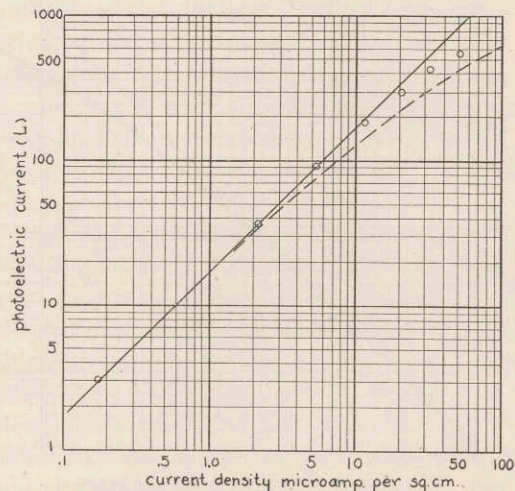

FIG. 7. Light output as a function of current density for the calcium-tungstate sample taken at 5000 volts applied. Phosphor potential 4300 volts to cathode. Dashed line willemite curve for comparison.

crease is even less than the first power.* This type of curve is particularly interesting in that it shows that if one were to use the rate of increase of light intensity with voltage as an indirect measure of the potential of the phosphor, the deductions on this basis would be decidedly in error, since direct measurements indicated that the potential of the phosphor throughout the entire observable range differed very little from that of the anode, and yet the rate at which the light output increased with voltage might be taken mistakenly as an indication that the potential of the phosphor had remained fixed at some relatively low voltage.

FIG. 8. Circles show light output per unit electron current as a function of the phosphor potential for calcium-tungstate. Crosses assuming a "dead voltage" of 100 volts. Straight line drawn with slope of two.

Properties of zinc-sulfide; silver activated

Silver activated zinc-sulfide was deposited on two of the test plates. These two samples were

---

* Dr. F. Seitz has suggested that this effect may be due to the excitation of x-ray levels in the cadmium atoms, with the resultant loss in electron energy, and therefore a decrease in the light-producing efficiency with increased voltage.
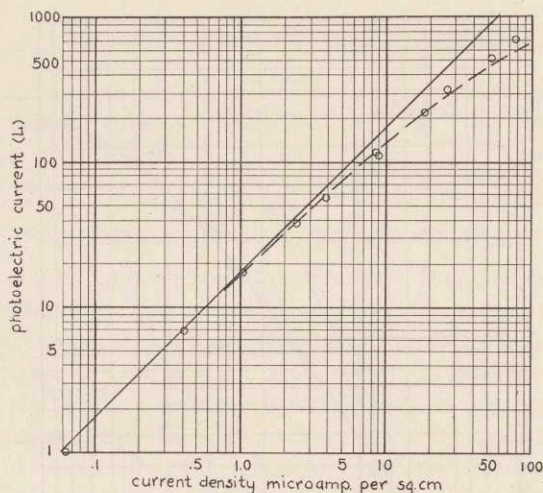
FIG. 9. Light output as a function of current density for the zinc-sulfide: cadmium-sulfide sample taken with 5000 volts applied. Phosphor potential 4970 volts. Dashed line is willemite curve for comparison.

similar in their behavior in all respects, and again showed that sulfides are good secondary emittors up to 10,000 volts and are probably able to go to much higher voltages than this. Another important property of these two samples of zinc-sulfide was that the light output per unit area was directly proportional to the current density to much higher values than for any other phosphor examined in this study. There was no detectable saturation effect up to 100 microamperes per sq. cm. At 3000 volts and with a sharply focused beam giving a current density of about ten milliamperes per sq. cm, the light output dropped to 40 percent of that expected on the assumption of perfect linearity between light output per unit area and current density. With this current density, willemite delivered only two percent of the expected light. Very extensive data were taken on these two phosphors because it was noticed that nearly all curves plotted showing the logarithm of the light output as a function of the logarithm of the current were good straight lines with a slope slightly in excess of unity. Some data showed an excess of as much as five or six percent. Since this was most noticeable with the lower anode voltages, where on account of the weakness of the light the errors are greatest, it must be assumed for the present that this apparent increase in light output above that expected was too near the limit set
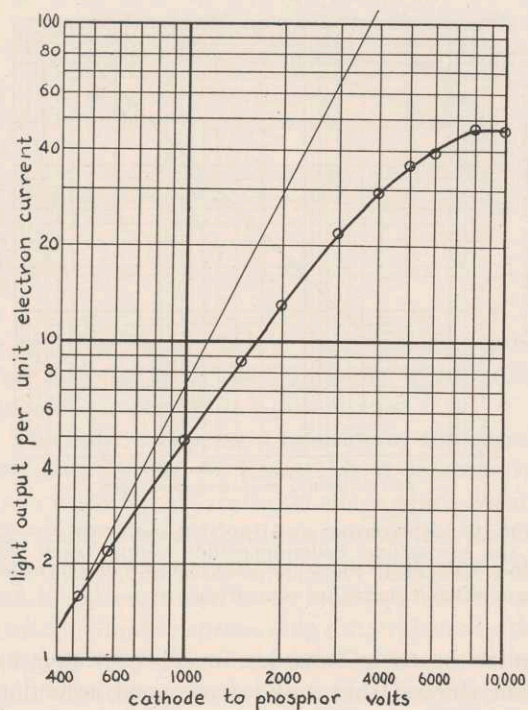
FIG. 10. Light output as a function of the electron energy for the zinc-sulfide: cadmium-sulfide sample. Straight line drawn with a slope of two.

by errors of measurement to be established without additional experiments.

Figure 11 shows the logarithm of the light output at constant current as a function of the logarithm of the electron energy in volts. The results obtained on both samples are shown, and, as is indicated, the slope observed on sample No. 1 was 2.8 while that for No. 2 was 2.9. These results were indeed surprising and can be taken as an indication that there must be some fundamental difference in the excitation process for zinc-sulfide as compared with willemite and calcium-tungstate. As long as the actual efficiency of the process in terms of watts input and light energy output is small, an increase in light output with the square of the voltage can be interpreted as showing that the number of excited centers produced per unit path length of the primary electron is independent of the electron energy, and therefore the light output is proportional to the penetration which, according to Leverenz,[4] is proportional to the square of the electron energy. A light output increasing more rapidly

—

[4] H. W. Leverenz, J. Opt. Soc. Am. **27**, 25 (1937).

than the square of the voltage may perhaps be an indication that excited centers are produced more efficiently by a high energy electron for each unit of path length.

SUMMARY OF RESULTS

As a result of these studies, the following conclusions seem to be justified.

(1) For low current densities the light output per unit area is accurately proportional to the current density. This is the equivalent of stating that for low current densities the light per unit of current is *constant*.

(2) With increased current density the light per unit current at constant voltage falls by an amount which depends primarily on the current density. The function representing this relation is nearly independent of the bombarding voltage. The slight dependence seems to be in the direc-
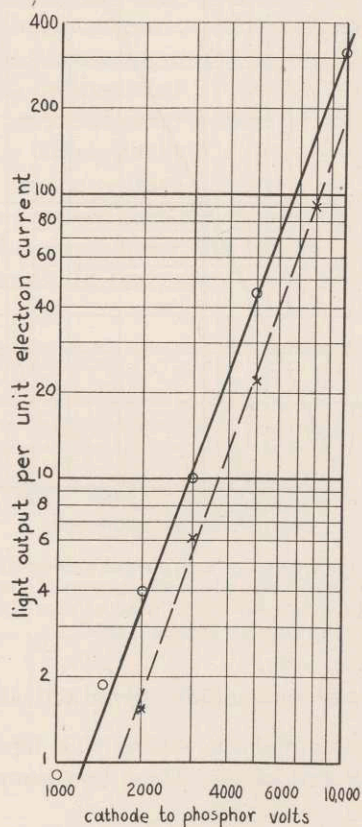

FIG. 11. Light output as a function of the electron energy for two samples of zinc-sulfide. Solid line for No. 1 and dashed line for No. 2. Straight lines drawn with slopes of 2.8 and 2.9. (The vertical separation is not significant.)

tion of a smaller saturation effect as the voltage is increased. A twenty percent loss in light per unit current was observed at the current densities given in Table II for the various phosphors.

(3) Except for the zinc-sulfide : cadmium-sulfide phosphor, the light per unit current at low densities, as a function of the electron energy V, was well represented by the empirical equation $(L/i) = A(V-V_0)^n$, where L/i is the light per unit current, A a constant, V_0 the so-called "dead voltage," generally zero, and n an exponent characteristic of the phosphor, tabulated in column three of Table II.

(4) Secondary emission properties of insulated phosphors operated in high vacuum determine the maximum useful operating voltage as discussed at length in the previous paper.[1] For conditions which are thought to correspond to the uncontaminated state of the materials, the upper limits of potential are given in column four of Table II.

For the opportunity to carry through the experiments upon which this paper is based, I am

TABLE II.

PHOSPHOR		MICROAMP. PER SQ. CM FOR 20% LOSS IN LIGHT	"n," POWER OF VOLTAGE FACTOR	MAXIMUM LIMITING VOLTAGE
CRYSTAL	ACTIVATOR			
$2(ZnO)SiO_2$	Mn	10	2	6500
ZnS; CdS	Ag	10	variable	>10,000
$CaWO_4$		30	2	5000
ZnS	Ag	200	2.8	>10,000