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## Boride Cathodes\*

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The thermionic emission properties of the borides of the alkaline-earth and rare-earth metals and thorium have been investigated. These compounds all have the same formula  $MB_6$  and the same crystal structure consisting of a three-dimensional boron framework in whose interlattice spaces the metal atoms are embedded. The valence electrons of the metal atoms are not accepted by the  $B_6$  complex, thus giving rise to the presence of free electrons which impart a metallic character to these compounds. This, together with the strong bonds between the boron atoms in the framework, produces a series of compounds which have high electrical conductivities and high thermal and chemical stabilities—ideal properties for a cathode material. When this structure is heated to a sufficiently high temperature, the metal atoms at the surface evaporate away. They are, however, immediately replaced by diffusion of metal atoms from the underlying cells. The boron frame work does not evaporate but remains intact. This process gives a mechanism for constantly maintaining an active cathode surface. Thermionic emission measurements made on these materials show the rare-earth metal borides to be superior

to the others. The highest emission was obtained from lanthanum boride. Its emission constants for the Dushman equation were  $\phi=2.66$  volts and  $A=29$  amps/cm<sup>2</sup>/degK<sup>2</sup>. This is higher than the emission normally obtained from thoria. Lanthanum boride has a relatively low evaporation rate corresponding to a latent heat of evaporation of 169 kilocalories per mole. If the hexaborides are operated at high temperature in contact with the refractory metals, boron diffuses into their metal lattices forming interstitial boron alloys with them. When this occurs, the boron framework which holds the alkaline-earth or rare-earth metal atoms collapses, permitting the latter to evaporate. However, the hexaboride cathodes may be operated at high temperatures in contact with tantalum carbide or graphite. Lanthanum boride cathodes are especially useful in applications where high current densities are required. They are also suitable for high voltage applications because they stand up well under positive ion bombardment. Since they are atmospherically stable and activate easily, they have found wide use in experimental demountable systems.

### I. INTRODUCTION

**I**N keeping pace with the trend towards higher and higher frequencies, the tube designer is continually confronted with the problem of extracting larger current densities from cathode surfaces. The problem has become so critical that electron emission efficiency is sacrificed in order to use cathode materials which will supply the requisite current densities and have a reasonable life. In many cases, even the latter is difficult to obtain. Three types of cathodes are now in common use. They are (1) clean metals, (2) metals with contaminated surfaces, and (3) nonmetallic electron emitters.

Type (3) make the most efficient cathodes, but cannot be operated at high direct current density levels because of the excessive evaporation of the materials which contribute to their high thermionic activity.

With regard to type (1), it is found that those elements provided by nature which are the best electron emitters also evaporate most readily. When such metals as cesium, barium, cerium, or thorium are heated to temperatures high enough to give electron emission currents of a few amperes per square centimeter, the evaporation rate becomes so high as to make the cathode useless in high vacuum devices. The refractory metals have poor emission efficiencies, but have more favorable evaporation rates. Figure 12 shows the evaporation rates of various refractory metals when they are heated to temperatures necessary to produce a given current density. The more efficient emitters would be located many decades above the refractory metals on this graph.

If these same metals, cesium, barium, cerium, or thorium are deposited on a refractory base metal such as tungsten in the form of films only one atom thick, these atoms become polarized to some extent and reduce the work function of the emitter below the value characteristic of the adsorbed metal in bulk. It is found that the evaporation rate of the atoms from the monolayer is much less than from the metal in bulk. These emitters may be classified as type (2) mentioned above. They form a much more desirable cathode for high current density applications.

Long life may be obtained from these cathodes providing some mechanism is provided for replacing those atoms in the monolayer which evaporate away or are sputtered off by high velocity positive ion bombardment due to residual gas in the tube. Considerable thought and ingenuity has been devoted to methods of accomplishing this. Some methods use an independent source which continually evaporates the active material onto the cathode surface. Other methods depend on the continuous decomposition of a compound to supply the active material. The diffusion rates of active materials through various substances have also been used in maintaining the monolayer. Still other methods use various combinations of these.

All of these methods have one inherent disadvantage in that there is no means for automatically regulating the rate of replacement of the active material. To insure an active cathode at all times, the rate of replacement must exceed the rate of loss from the monolayer. This results in a waste of active material.

It has been found possible to overcome this difficulty and to provide a cathode with many other advantageous properties by embedding the alkaline-earth or rare-

\* This paper was presented at the Autumn Meeting of the National Academy of Sciences in Schenectady on October 11, 1950.

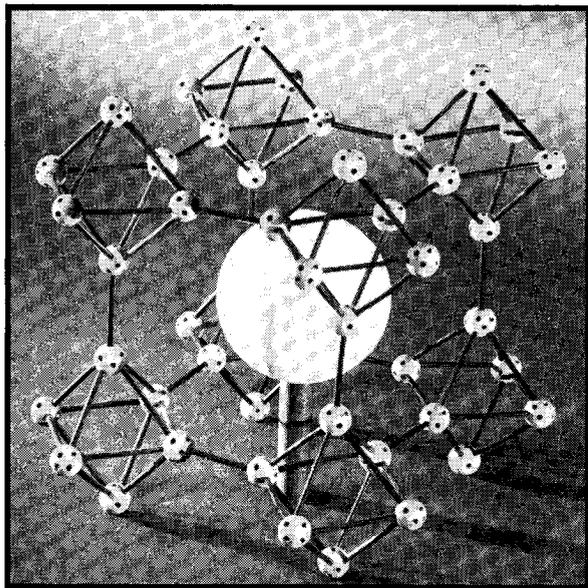


FIG. 1. The hexaboride crystal structure. The boron atoms form a three-dimensional framework which surrounds the large metal atoms.

earth metals or thorium in a matrix of boron. An understanding of how this is accomplished may be easily obtained by considering the unusual properties of a series of interstitial compounds of boron and the alkaline-earth or rare-earth metals or thorium. These all form borides with the same formula and have the same crystal structure. Although some of these compounds were made over 50 years ago and their crystal structure determined nearly 20 years ago, they appear to have found little application other than to arouse the curiosity of the crystallographer.

## II. HEXABORIDE PROPERTIES

The alkaline-earth metals, the rare-earth metals, and thorium form borides of the type  $MB_6$ . These compounds all have the same cubic crystal structure as shown in Fig. 1. The small boron atoms form a three-dimensional framework structure which surrounds the large metal atoms. The boron framework is made up of octahedra, one at each corner of the cube. These are bonded together at their apexes. Each boron atom has four adjacent neighbors in its own octahedron and another neighbor in the direction of one of the cubical main axes, thus giving a homopolar lattice structure with the coordination number 5. Each boron atom has its three valence electrons distributed over five bonds.

The metal atoms trapped in the boron cages have a coordination number of 24. It would appear, however, that there are no valence bonds between the metal atoms and the surrounding boron atoms. The valence electrons of the metal atoms thus become free electrons and impart a metallic character to the compounds.

It would appear from Table I that the lattice constants of the hexaborides are determined primarily by

the boron frame work structure and not by the size of the embedded metal atoms. The radii of the metals, which can be calculated from these lattice constants, vary but little, notwithstanding the fact that the radii of these atoms in the elementary as well as in the ionized state have very different sizes. It would thus appear that the lattice constant of the three-dimensional framework remains substantially constant during the isomorphous exchange of the metal atoms as long as they remain smaller than the interlattice spaces. If the metal atoms become larger, the framework will expand to accommodate them as is shown by the  $BaB_6$ .

The strong binding forces between the boron atoms lead to a series of compounds which are very refractory, with melting points above  $2100^\circ\text{C}$ . The melting points of the hexaborides are characteristic of the boron structure and not of the metal atoms. Table I shows that the variation in the melting points is less than 4 percent.

The borides are very stable chemically; moisture, oxygen, and even hydrochloric acid do not react with them. The hexaborides are opaque. The alkaline-earth metal borides are black and brownish black. The rare-

TABLE I. Lattice constants<sup>a</sup> and melting points of the hexaborides.

Boride	$a_0$	mp
$CaB_6$	4.145A	2235°C
$SrB_6$	4.19A	2235°C
$BaB_6$	4.28A	2270°C
$LaB_6$	4.145A	2210°C
$CeB_6$	4.129A	2190°C
$ThB_6$	4.15A	2195°C

<sup>a</sup> M. V. Stackelberg and F. Neumann, *Z. physik. Chem.* **19B**, 314 (1932).

earth borides are various shades of blue and purple. When dry,  $LaB_6$  is a reddish purple, but turns a deep red when moist.

The metallic character of these compounds is evident from their high electrical conductivity. Figure 2 shows the specific resistance of well-sintered  $LaB_6$  as a function

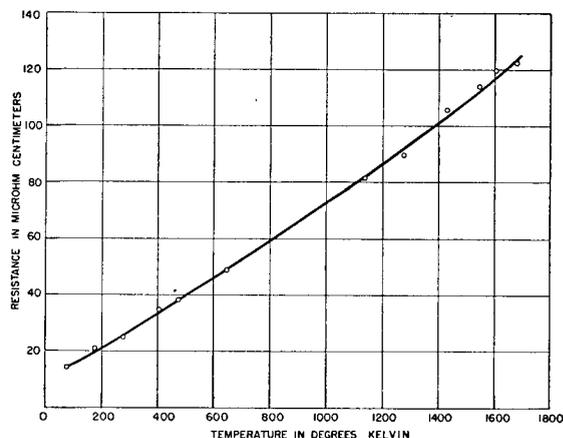


FIG. 2. The specific resistance of sintered  $LaB_6$  as a function of the absolute temperature. The sample was sintered at  $1850^\circ\text{C}$  for  $\frac{1}{2}$  hour.

tion of temperature. The resistance is approximately the same as that of lead. The resistance-temperature coefficient is positive, like that of a metal. This is true of all the hexaborides. Calcium boride has the highest specific resistance of all the hexaborides, as might be expected because of the small diameter of the calcium atom.

The thermoelectric power of  $\text{LaB}_6$  measured against annealed Baker's platinum was found to be 8 microvolts per degree centigrade. These measurements were made over the temperature range 100 to 300 degrees centigrade. The polarity was such that the electron current flow was from the cold junction to the hot junction through the boride.

Hall effect measurements<sup>1</sup> made on  $\text{LaB}_6$  also show its metallic properties. A  $\text{LaB}_6$  bar 1.261 by 0.588 by 0.151 centimeters was made from pressed powder and sintered in vacuum at 1800°C for 15 minutes. The density was 2.61 grams/cm<sup>3</sup>. The specific resistance was found to be  $\rho = 57 \times 10^{-6}$  ohm centimeters and the Hall coefficient  $R = 7.7 \times 10^{-12}$  volt centimeters/ampere gauss. The mobility of the current carriers is calculated from the relation  $(R/\rho) \times 10^8$  and found to be 13.5 centimeters/second per volt/centimeter. This value is not uncommon for metals. The density of the carriers is given by the relation  $n = 6.3 \times 10^{10}/R$  and found to be  $8.2 \times 10^{21}$  per cubic centimeter or  $6.4 \times 10^{23}$  per mole of  $\text{LaB}_6$ . This is approximately Avogadro's number, indicating that there is one free electron for every lanthanum atom. In their magnetic investigations of  $\text{LaB}_6$ , Klemm, Schüth, and Stackelberg<sup>2</sup> found triply ionized lanthanum.

When the hexaborides are heated to a sufficiently high temperature, the metal atoms at the surface evaporate away. They are, however, immediately replaced by diffusion of metal atoms from the cells below. The boron framework does not evaporate, but remains intact. It is found that this diffusion of metal atoms to the surface occurs only when there is a vacancy at the surface. This property keeps evaporation losses at a minimum and at the same time provides a mechanism for constantly maintaining an active cathode surface. This, together with the high electrical conductivity and high thermal and chemical stability, gives ideal properties for a cathode material.

### III. CHEMICAL PREPARATION

The borides of Ca, Sr, and Ba were first obtained by Moissan and Williams<sup>3</sup> by reducing the borates with aluminum in an arc furnace. An improved method is given by Andrieux.<sup>4</sup> He electrolyzed a molten mixture of the borate and fluoride of the metals in question at

<sup>1</sup> The writer is indebted to Dr. W. C. Dunlap, Jr., of this laboratory for these data.

<sup>2</sup> Klemm, Schüth, and Stackelberg, *Z. physik Chem.* **19B**, 321 (1932).

<sup>3</sup> H. Moissan and P. Williams, *Compt. rend.* **125**, 629 (1897).

<sup>4</sup> L. Andrieux, *Compt. rend.* **182**, 126 (1926); **184**, 91 (1927); **186**, 1537 (1928); **186**, 1736 (1928).

1000°C. Stackelberg and Neumann,<sup>5</sup> in their study of the  $\text{MB}_6$  crystal structure, have also prepared the borides of the alkaline earth and rare-earth metals by the method of Andrieux.

In our work, the borides were prepared from the metal or the metal hydride and amorphous boron. Fresh metal, in the form of powder or filings, was mixed with the amorphous boron powder and pressed into bars 1 by 1 by 6 inches with a 50-ton press. These bars were placed in a graphite crucible and packed with boron powder. This was fired in an electric furnace in a pure dry hydrogen atmosphere for 1 hour at 1375°C. The boron powder was removed, and hydrogen firing was continued in a graphite crucible in an induction furnace for 20 minutes at 1800°C. The boride thus obtained was crushed, washed in HCl, rinsed in water, and ground dry in a steel ball mill. The powder thus obtained was washed in concentrated hydrochloric acid to remove any free metal, metal oxide, and boric oxide. It was then washed in distilled water several times until all traces of the acid were removed. Small amounts of free boron could be removed to a large extent by stirring the powder in distilled water and then decanting off the water before the powder completely settled out. (The rare-earth borides are approximately 2.5 times as dense as amorphous boron.)

The powder is then dried and is ready for use. It may be pressed into any desired shape and sintered in hydrogen or vacuum. Sintering at 1375°C for 15 minutes gives a material which is soft enough so that it may be machined. Sintering at 1800°C for 15 minutes gives a material which is very hard and about 0.5 the theoretical density.

The metals used in preparation of the borides were quite pure, usually about 99 percent with traces of Fe, Cr, Ni, and Si. The boron, however, was not very pure and contained large amounts of Mg, Si, and Al with traces of Pb, Sn, Fe, Mn, and Cu. A large amount of these impurities are distilled out in the preparation of the boride; and spectrographic tests made on the final boride show that silicon is present, but only traces of Fe, Al, Mg, and Mn.

### IV. ELECTRON EMISSION CONSTANTS

In measuring the electron emission constants of the borides, one is confronted with two problems. One is the establishment of temperature scales for the various materials and the other is the prevention of their coming in contact with metals which react chemically with them (Section V) when they are heated. These difficulties were avoided by making a boride cathode in the form of a self-supporting hollow rod, as shown in Fig. 3. The three tungsten coils which surround the rod are used for heating it and for collecting the electron emission from it. The two end coils are connected in series. The heater currents through them and the center coil

<sup>5</sup> M. v. Stackelberg and F. Neumann, *Z. physik Chem.* **19B**, 314 (1932).

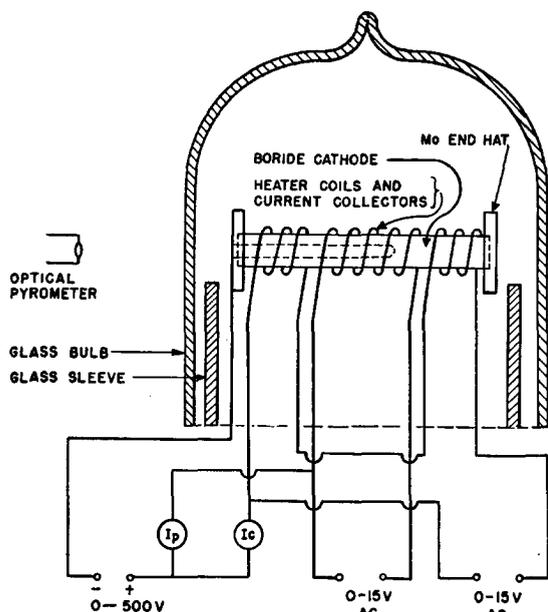


FIG. 3. Experimental tube setup for determining the emission constants of sintered borides.

are adjusted so that the rod, as viewed through the hole, appears to be uniformly bright throughout the major portion of its length. Since the radiation from the cavity is sensibly blackbody radiation, the temperature may be read directly with a pyrometer without emissivity correction. Further, since the rod is heated by radiation from the surrounding coils, its temperature is uniform throughout and the temperature as measured at the inside cavity walls is the same as that at the outer surface.

The three coils are made positive with respect to the rod and are used to collect the electron emission current. The electron current collected by the center coil from the uniform temperature portion of the cathode

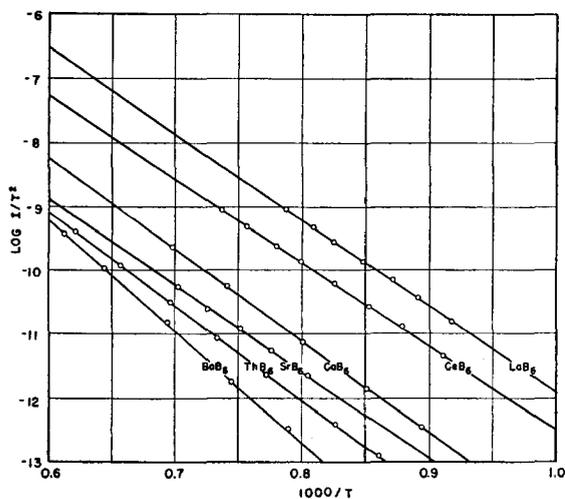


FIG. 4. Richardson plots for the alkaline-earth, rare-earth, and thorium borides. The emission constants are given in Table II.

is measured by the  $I_p$  meter. The end coils are connected to the positive voltage source through a similar meter  $I_c$  and serve as guard rings, collecting the emission current from the end portions of the rod. The construction and processing of the tubes used in the present measurements follows.

The boride rod was 180 mils in diameter and  $1\frac{1}{8}$  inches long. The rod was made by sintering the pressed boride powder for 15 minutes at  $1375^\circ\text{C}$ . The surface was then ground in a centerless grinder to give a uniform diameter of 180 mils. A 93-mil hole was drilled in one end to a depth of  $\frac{3}{4}$  inch. The rod was cut to a length of  $1\frac{1}{8}$  inches and placed in position between the molybdenum end hats. The heater coils were made from 20-mil tungsten wire wound on a 307-mil diameter mandrel 28 turns per inch. The center coil was  $\frac{1}{2}$  inch long and the end coils were  $\frac{1}{4}$  inch long.

The tube was baked out for one hour at  $450^\circ\text{C}$  and the cathode outgassed on the pump by operation at  $1500^\circ\text{C}$  to  $1600^\circ\text{C}$ . During these operations, a glass sleeve (Fig. 3) protected the bulb from any discoloration at the place through which pyrometer measurements were to be made. Two barium getters were flashed and the tube sealed off. The tube was operated several hours at a temperature greater than that at which data was taken, to insure stable emission.

The electron emission from the various borides was measured as a function of their temperature with a

TABLE II. Hexaboride emission constants as determined from the data in Figs. 4 and 5.

Boride	$A$ (amps/cm <sup>2</sup> /degK <sup>2</sup> )	$\phi$ (volts)
CaB <sub>6</sub>	2.6	2.86
SrB <sub>6</sub>	0.14	2.67
BaB <sub>6</sub>	16	3.45
LaB <sub>6</sub>	29	2.66
CeB <sub>6</sub>	3.6	2.59
Misch metal boride	14	2.64
ThB <sub>6</sub>	0.5	2.92

constant potential of 500 volts between cathode and collector. Richardson plots were made from these data, using the thermionic emission equation

$$\log_{10} I/T^2 = \log_{10} A - 11600\phi/2.303T, \quad (1)$$

where  $I$  is the current density in amperes per cm<sup>2</sup>,  $T$  the absolute temperature in degrees Kelvin,  $A$  is an empirical constant expressed in amperes per cm<sup>2</sup> per degree Kelvin<sup>2</sup>, and  $\phi$  is the conventional work function expressed in volts.

Figure 4 shows a series of Richardson plots for the alkaline-earth, rare-earth, and thorium borides. Straight lines were obtained in all cases, showing  $\phi$  to be substantially independent of temperature. It will be noted that the rare-earth borides are better emitters than the alkaline-earth or thorium borides. Values of  $A$  and  $\phi$  obtained from Fig. 2 are given in Table II.

Figure 5 shows the emission obtained for some mixed borides of the rare-earth metals. X-ray analysis of the crystal structure of these mixed borides shows that they form solid solutions over the entire composition range. Misch metal, which is an alloy of all the rare-earth

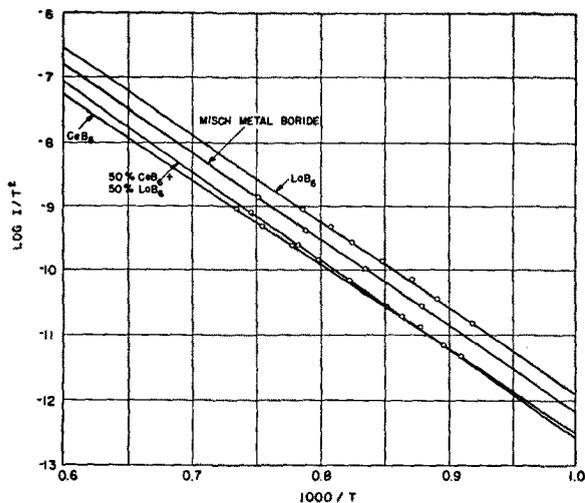


FIG. 5. Richardson plots for some mixed borides of the rare-earth metals. Misch metal boride is a hexaboride made from misch metal—an alloy of the rare-earth metals.

metals, forms a solid solution of mixed borides with an electron emission only slightly less than that of  $LaB_6$ . This is of commercial interest since misch metal is considerably cheaper than lanthanum metal.

Figure 6 shows the emission obtained from solid solutions of cerium and barium borides of various compositions. Figure 7 shows similar data for cerium and thorium borides. It will be observed that the mixed borides give emission currents which fall within the limits of emission established by the pure components. This result is in accordance with the theoretical considerations stated in Sec. VII.

It is of interest to compare the emission from  $LaB_6$ , the best boride emitter, with some of the conventional cathode materials. This is shown in Fig. 8. The emission from  $LaB_6$  is surpassed only by barium oxide at low temperatures. In the high current density range,  $LaB_6$

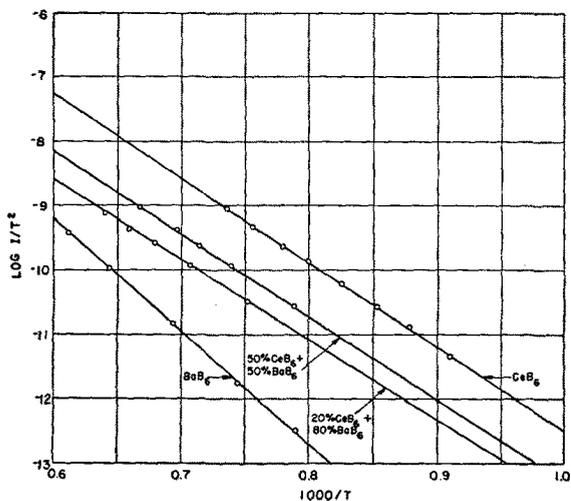


FIG. 6. Richardson plots for mixed borides of cerium and barium in solid solution.

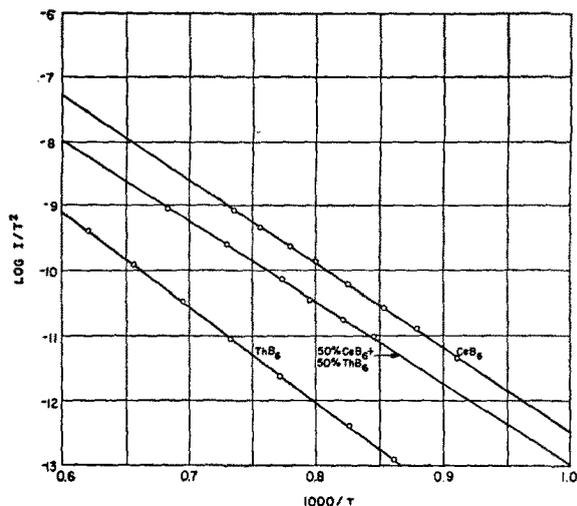


FIG. 7. Richardson plots for mixed borides of cerium and thorium.

is superior to any of the conventional materials now available.

V. CATHODE PREPARATION AND BASE MATERIALS

When the hexaborides are heated in contact with refractory metals such as W, Mo, Pt, Cb, or Ta, the boron atoms diffuse into these metal lattices, taking up positions in the interstices and forming interstitial boron alloys with them. When boron diffusion starts, the boron frame work which holds the alkaline-earth or rare-earth atoms collapses, permitting the latter to evaporate. This process will continue until all of the interstices of the base metal are filled with boron or until all of the boron from the hexaboride coating is used up.

The rate at which this diffusion process proceeds is indicated in the following experiment. A filament was

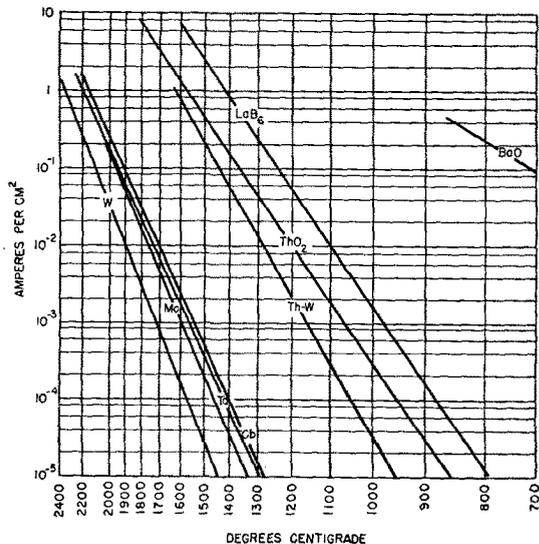


FIG. 8. Electron emission of some common cathode materials and lanthanum boride plotted as a function of the temperature.

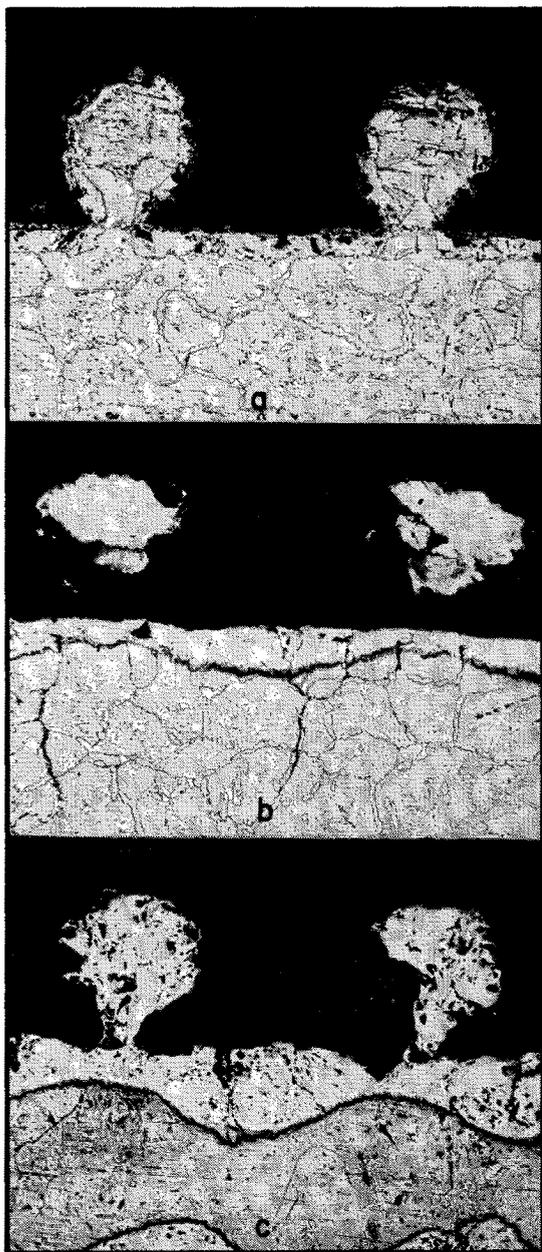


FIG. 9. Photo-micrographs showing cross section of an overwound tantalum filament. In (a) the filament has been carbonized at the surface to a depth of approximately one mil. In (b) the carbonized filament has been heated to 2000°C in contact with boron. In (c) an uncarbonized filament was given the same treatment as in (b).

made with a 20-mil diameter tungsten wire core overwound with 10-mil diameter wire with a 10-mil space between the overwound turns. The space between the turns was filled with  $\text{LaB}_6$ . The cathode was operated at 1515°C and gave very good emission. At the end of 48 hours, however, the emission had ceased and there was no  $\text{LaB}_6$  visible on the overwound tungsten wire. The bulb was covered with a brown deposit which was mostly lanthanum. The tungsten showed a slight swell-

ing and was very brittle, crumbling into very small pieces when handled. A microscopic examination showed many small cracks in the metal. A spectrographic analysis of the filament showed only tungsten and boron present, lanthanum being entirely absent.

Looking at this problem from the interstitial solid solution point of view, an effective way to prevent boron from diffusing into the base metal is to previously fill the interstices with small atoms before it is brought in contact with the boride at high temperatures. The metalloids, boron and carbon, are most suitable for this purpose.

If the cathode is to be made by completely boronizing or carbonizing the base metal, the rate of diffusion of the metalloids in the base metal is of little importance, since the evaporation rates of the metalloids are negligible at the cathode operating temperature. However, completely boronizing or carbonizing the base metal always results in a very brittle alloy; and for some applications, such as filaments, this may prove to be a severe limitation in handling. It would be better, therefore, just to boronize or carbonize the surface of the base metal, leaving a ductile core. In this case, the diffusion rate of the metalloid into the base metal becomes important. If the diffusion is appreciable at the operating temperature of the cathode, the volume near the surface of the base metal will be depleted of metalloid atoms, leaving vacant interstices into which the boron will diffuse from the hexaboride resulting in its dissociation. It follows that boron cannot be used in cases where a ductile core is required because of its high diffusion rate in the base metal. If this were not so, the boride would require no protective barrier.

Tests made on the refractory metals show that the diffusion of boron and carbon is slowest in tantalum. Overwound tantalum filaments were carbonized by packing them in finely powdered sugar charcoal in a graphite crucible and heating in vacuum for one minute at 2300°C. This gives a tantalum carbide coating of about one or two mils thickness.<sup>6</sup> At 1500°C, this coating is extremely stable and prevents the boron from diffusing into the tantalum.

Figure 9 shows some photo-micrographs of a 20-mil diameter tantalum wire overwound with 10-mil diameter tantalum wire. These were cross sectioned, polished, and etched, to show the carbide and boride surfaces. Figure 9a shows a sample which was carbonized at the surface as described above. Figure 9b shows a carbonized sample which was heated for 5 minutes at 2000°C in contact with boron. Figure 9c shows a sample which was not carbonized, but was heated for 5 minutes at 2000°C in contact with boron. It can be seen that in the unprotected sample, the boron has diffused entirely through the overwinding and nearly half-way through the core wire.

<sup>6</sup> The carbonizing could have been done equally well or better in a hydrocarbon atmosphere.

An unprotected overwound tantalum wire coated with  $\text{LaB}_6$  and operated at  $1515^\circ\text{C}$  for 144 hours showed diffusion of boron into the tantalum for a depth of approximately 3 mils. On carbonized tantalum, no evidence of boron diffusion was found under similar operating conditions.

It was also observed that the borides do not react with graphite. Many cathodes have been made by putting the boride in graphite cups or by sintering it on graphite cylinders and plates which have scored or undercut surfaces. Graphite may also be used as a boron barrier on filaments.<sup>7</sup>

Although the borides will sinter by themselves at temperatures as low as  $1400^\circ\text{C}$ , they do not adhere well to metal or ceramic surfaces. For this reason, they cannot be applied to cathode base materials in the conventional way that the carbonates or thoria are applied. The borides may be applied to form flat cathode surfaces by drilling, grooving, or fastening a coarse mesh to the base material. These methods provide surfaces into which the boride may lock. Filamentary boride cathodes are made by overwinding the filament core wire with another wire  $\frac{1}{2}$  its diameter. The space between turns of the overwound wire is made equal to its diameter, and is then filled with boride.

The boride powder is mixed with amyl acetate to form a thin paste which is painted on the cathode base material. The cathode is then sintered in vacuum for 15 minutes to one hour at temperatures ranging from  $1700^\circ\text{C}$  to  $1800^\circ\text{C}$ .

Solid boride cathodes may be made in the form of disks, rods, etc., by pressing the powder into the desired shape and sintering in vacuum. Unusual shapes may be formed by the use of graphite molds. The mold is filled with boride paste and sintered. After firing, the cathode can be easily removed from the mold, since there will be some shrinkage of the boride and there will be no bonding between the latter and the graphite.

## VI. EVAPORATION RATE OF LANTHANUM BORIDE

The usual method for determining the evaporation rates of highly refractory metals is to observe the rate of loss in weight of filaments operated at constant temperatures. This method presents several difficulties when applied to the borides. At the present state of the art, these compounds cannot be made into wires. If a refractory metal wire is coated with the boride, there is always danger of chemical reaction between the two at high temperatures. If sintered boride rods are used, there is the problem of uniform heating, and an accurate determination of the temperature is difficult. Another factor which makes the rate of loss in weight method undesirable when applied to cathodes is that all measurements must be made at temperatures considerably higher than the operating temperature. The data ob-

<sup>7</sup> Mr. M. L. Perl of the Electronics Department of the General Electric Company has developed a process for depositing a tenacious layer of carbon on ductile tantalum wire.

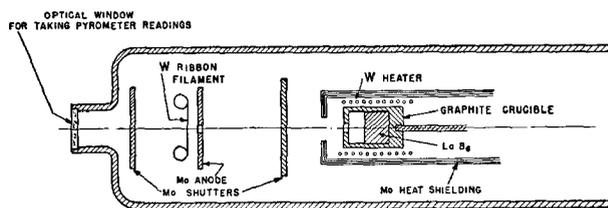


FIG. 10. Schematic diagram of the tube used for measuring the evaporation rate of lanthanum boride.

tained must then be extrapolated over several decades to apply at normal operating temperatures. This may introduce considerable error.

The method described below has the advantage that the true temperature of the sample may be read directly with an optical pyrometer; no weighing or chemical analysis is necessary, and readings may be taken near the operating temperature in relatively short times. This method may be used to measure the evaporation rate of any material whose evaporation product forms an active thermionic surface.

A schematic diagram in Fig. 10 illustrates the method used. The  $\text{LaB}_6$  is placed in a graphite crucible which does not react with it at high temperatures. There is a small opening in the end of the crucible through which the lanthanum can evaporate. The crucible is heated by a closely wound tungsten coil which surrounds it. Several layers of thin molybdenum foil are placed around the whole assembly to act as heat shielding and to give a uniform distribution of temperature throughout the crucible. The lanthanum evaporating from the crucible passes through the hole in the molybdenum anode and condenses on the tungsten ribbon. This ribbon is operated at about  $800^\circ\text{C}$  so that the rate of evaporation of lanthanum atoms from a single layer on the surface is negligible. The anode is made 100 volts positive with respect to the ribbon.

When the crucible has been heated for a time sufficient to reach an equilibrium temperature, the molybdenum shutter is opened and the lanthanum allowed to condense on the ribbon. The electron emission from the ribbon to the anode is recorded as a function of time on a photoelectric recorder. The length of time for the emission current from the ribbon to reach a maximum is measured. This corresponds to the time required for a monolayer of lanthanum to deposit on the ribbon. The temperature of the  $\text{LaB}_6$  is measured with an optical pyrometer by opening both shutters and reading the temperature inside the crucible. Only a correction for the window need be made, since the radiation from the crucible is essentially blackbody radiation.

The rate of evaporation of lanthanum from the  $\text{LaB}_6$  can be computed as follows. Clausing<sup>8</sup> has shown that the number of atoms per second per unit solid angle leaving the crucible in the direction of the hole axis is  $\nu r^2$ , where  $\nu$  is the number of atoms striking the crucible wall per square centimeter per second and  $r$  is

<sup>8</sup> P. Clausing, *Z. Physik* **66**, 471 (1930).

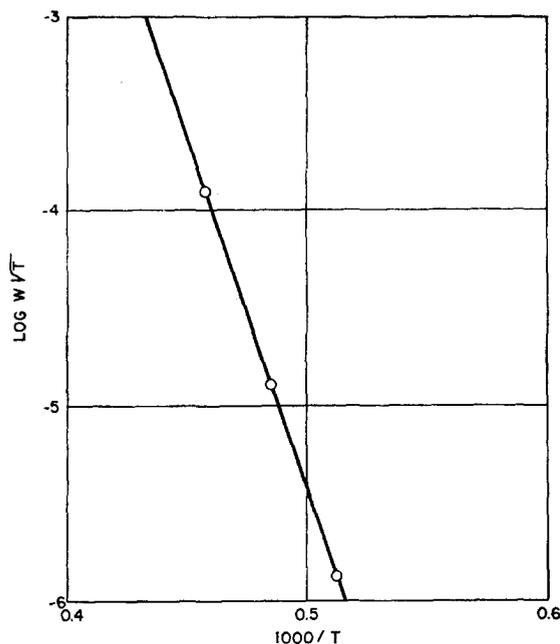


FIG. 11. Evaporation rate data for lanthanum boride.

the radius, in centimeters, of the hole in the crucible. The number of atoms per square centimeter falling on the ribbon in time  $t$  is  $\nu r^2 t / R^2$ , where  $R$  is the distance between the ribbon and the opening in the crucible. If  $N_0$  is the number of lanthanum atoms per square centimeter required to give a monolayer on the tungsten ribbon, then the number of atomic layers deposited on the ribbon in time  $t$  is  $\nu r^2 t / R^2 N_0$ . If  $t$  is the time required to deposit a monolayer, then on equating this expression to unity and solving for  $\nu$ , it becomes

$$\nu = R^2 N_0 / r^2 t. \quad (2)$$

This is the number of lanthanum atoms leaving the  $\text{LaB}_6$  surface per square centimeter per second. Expressed in grams per square centimeter per second, this quantity becomes

$$W = M R^2 N_0 / N_A r^2 t, \quad (3)$$

where  $M$  is the atomic weight of lanthanum and  $N_A$  is Avogadro's number.

The uncertainty in  $N_0$  will cause the greatest error in calculating  $W$  from Eq. (3). The absorbed lanthanum atoms will no doubt arrange themselves in conformity with the underlying tungsten lattice. However, the lanthanum atoms are too large to form a one-to-one correspondence with the tungsten atoms. A one-to-two

TABLE III. Evaporation rate data for lanthanum boride.<sup>a</sup>

$T$ ( $^{\circ}\text{K}$ )	$t$ (sec)	$W$ (gm/cm <sup>2</sup> /sec)
2183	2700	$2.66 \times 10^{-6}$
2063	25,800	$2.78 \times 10^{-7}$
1953	248,400	$2.89 \times 10^{-8}$

<sup>a</sup>  $R = 6.47$  cm.  $r = 0.0381$  cm.

or one-to-three relationship would be more probable. Further, it is believed that the maximum electron emission occurs when the concentration of the absorbed atoms is somewhat less than a complete monolayer. Also, the actual surface area of thermally etched tungsten will be greater than the projected area because the surface consists of many crystal faces inclined to the original surface. Since the interest here is in determining lanthanum boride cathode life, it will be better to assume a value for  $N_0$  which is somewhat large. If the closest possible packing of the lanthanum atoms on a plane surface is assumed, a value of  $8.33 \times 10^{14}$  atoms per square centimeter is obtained. (This is not appreciably different than  $7.13 \times 10^{14}$ , which is the number of absorbed atoms per square centimeter for a one-to-two correspondence on dodecahedral tungsten crystal faces.) If this value is multiplied by 1.3 to allow for orientation of the tungsten crystal faces,<sup>9</sup> a value of  $1.08 \times 10^{15}$  atoms per square centimeter is obtained for  $N_0$ .

Table III shows the time required to obtain maximum emission at various crucible temperatures and the evaporation rates computed from Eq. (3).

The evaporation rate of most substances may be expressed by the relation

$$\log W = C - \frac{1}{2} \log T - (B/T), \quad (4)$$

where  $W$  is the rate of evaporation in grams per square centimeter per second at a temperature  $T$  degrees absolute, and  $C$  and  $B$  are empirical constants. If the data in Table III are plotted as  $\log W(T)^{1/2}$  vs  $1/T$ , a straight line should result if Eq. (4) applies. This is shown to be the case in Fig. 11. The following values of  $C$  and  $B$  were obtained from this curve:

$$C = 13 \quad \text{and} \quad B = 36,850^{\circ}\text{K}.$$

It should be noted that the value of  $B$ , which corresponds to a latent heat of evaporation of 169 kilocalories per mole, is not dependent on the geometry of the setup or the value assumed for  $N_0$ , but depends only on  $T$  and  $t$ .

A comparison of the evaporation rate of  $\text{LaB}_6$  with the refractory metals when used as electron emitters is shown in Fig. 12. These curves show the evaporation rates at temperatures which will give the emission current densities shown by the abscissas.

## VII. ACTIVATION AND EMISSION PHENOMENA

Boride cathodes require no activation in the usual sense of the word. If a  $\text{LaB}_6$  cathode, for example, is heated to  $1500^{\circ}\text{C}$  or  $1600^{\circ}\text{C}$  for a few minutes for outgassing, it is found to be completely active. In fact, it is impossible to outgas the cathode properly without making it active. However, it was found that  $\text{LaB}_6$  cath-

<sup>9</sup> L. Tonks, Phys. Rev. 38, 1030 (1931), has calculated a value of 1.225 for the ratio of the exposed crystal face area to the projected area for dodecahedral faces assuming random crystal orientation and minimum face excess.

odes, which had been washed in HCl and not previously heated in vacuum, were inactive at 1100°C.

The activation of  $\text{LaB}_6$  was investigated further in a special tube shown in Fig. 13.  $\text{LaB}_6$  powder was placed in a graphite cup heated by radiation from a surrounding tungsten coil. A graphite anode was placed inside the cup near the  $\text{LaB}_6$  as shown. The anode contained a small hole through which the temperature of the  $\text{LaB}_6$  could be measured with an optical pyrometer.

The  $\text{LaB}_6$  was heated at an activation temperature for a period of time, and its thermionic condition was checked frequently by dropping to a testing temperature of 1115°C and measuring the saturated emission. The saturated emission at 1115°C is plotted against the activation time for activation temperatures of 1375°C and 1430°C. The activation rate is approximately three times as large at the higher temperature.

An active  $\text{LaB}_6$  cathode opened up to the air and then evacuated again will be inactive when first heated to 1115°C. If it is heated for a few moments at 1500°C or 1600°C, it will return to its original activity.

When  $\text{LaB}_6$  is operated in vacuum for a long period of time at a high temperature, a brown deposit collects on the glass walls of the tube. An x-ray analysis shows this material to be amorphous. It is soluble in hydrochloric acid and a spectrographic analysis shows it to be mostly lanthanum. A microscopic examination of the  $\text{LaB}_6$  surface shows it to be clean with no residue present.

From these facts, it is concluded that the thermionic activity of the cathode is caused by the presence of lanthanum at the surface of the  $\text{LaB}_6$ . Whether this is a layer of lanthanum atoms on a  $\text{LaB}_6$  surface or simply a  $\text{LaB}_6$  surface is somewhat problematical because of the high concentration of lanthanum atoms in  $\text{LaB}_6$ . If  $\text{LaB}_6$  dissociated in the usual manner on heating, a residue of boron would be left on its surface, since the vapor pressure of boron is extremely small compared with lanthanum. Since none is found, it is concluded that lanthanum diffuses out through the boron framework and evaporates, while the boron structure remains intact. After prolonged operation at high temperatures, the  $\text{LaB}_6$  will become so depleted in lanthanum that the boron framework will collapse, leaving a boron coating on the cathode.

The nature of the thermionic activity and the lanthanum atoms at the surface of the  $\text{LaB}_6$  was investigated further by operating the cathode in mercury vapor. A graphite cylinder coated with  $\text{LaB}_6$  was heated by radiation from a tungsten coil within. The anode was connected to the positive side of a 110-volt line through a variable resistance.

With the cathode operated at 1500°C, the anode current would increase with a decrease in the anode series resistance. The anode drop was approximately 10 to 15 volts. When the anode current approached the temperature limited emission of the cathode, the anode voltage would rise and, at about 20 to 30 volts, the

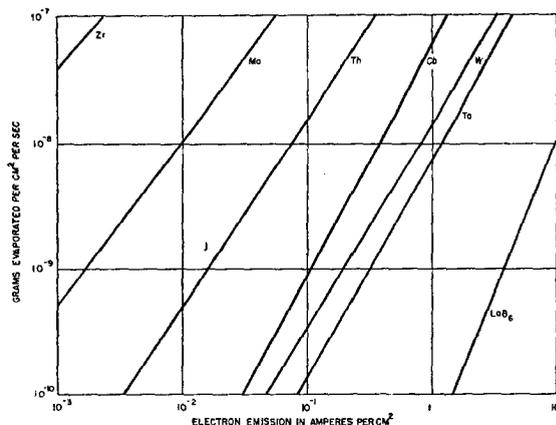


FIG. 12. Evaporation rate of various materials when they are heated to a temperature which will give the electron emission shown.

anode current would drop rapidly to a very low value with the anode voltage rising to nearly 110 volts. If the anode series resistance was now increased again to its former value, the cathode would activate immediately and the anode voltage would drop to its former value. This procedure could be repeated many times, always with the same results. When the cathode temperature was reduced to 1200°C, similar results were observed except that the cathode would not reactivate when the anode series resistance was increased again. The cathode could be activated again by heating momentarily to 1500°C.

From this, it is concluded that when the mercury ions exceed energies of approximately 20 electron volts, they readily sputter off the lanthanum atoms from the surface of the  $\text{LaB}_6$  and make the cathode inactive. However, at 1500°C, the lanthanum atoms diffuse very rapidly to the surface, making the cathode active again. At 1200°C, this diffusion is very slow and the cathode does not activate immediately.

The diffusion of lanthanum to the  $\text{LaB}_6$  surface, when a vacancy exists there, was investigated quantitatively as a function of the temperature. The  $\text{LaB}_6$  surface was first made inactive by bombardment with

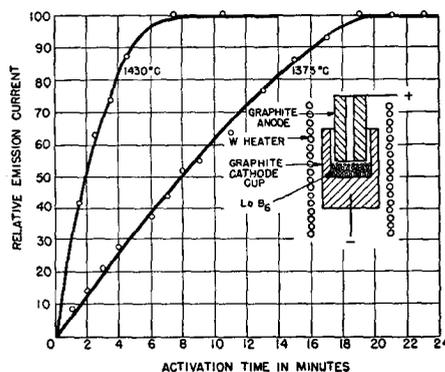


FIG. 13. Time variation of the emission at 1115°C from initially inactive lanthanum boride for two activating temperatures.

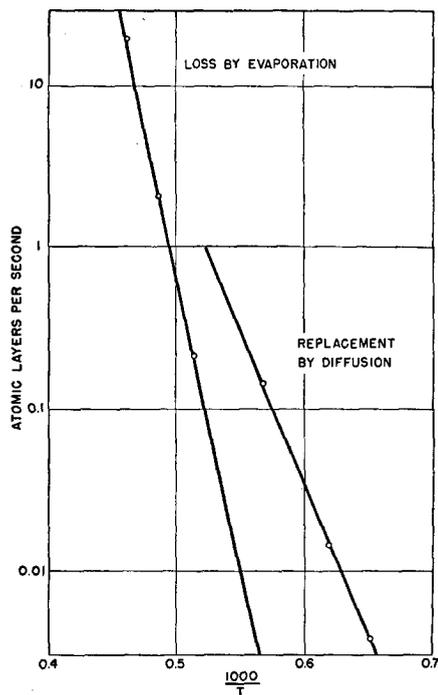


Fig. 14. Curves showing the rate at which lanthanum evaporates from the  $\text{LaB}_6$  surface and the rate at which it is replaced by diffusion.

110-volt mercury ions. The anode voltage was then immediately reduced to approximately 18 volts and the time for the emission to recover was measured. The reciprocal of this period is a measure of the average rate of diffusion of lanthanum to the surface in monolayers per second. The results of measurements at three different temperatures are plotted in Fig. 14. Also plotted in this same figure are the evaporation rate data of Table III expressed in atomic layers per second of lanthanum rather than grams per square centimeter per second. It thus appears that in the operating temperature range, the lanthanum on the  $\text{LaB}_6$  surface is replaced, when a vacancy occurs, at a much faster rate than the lanthanum would normally evaporate from the  $\text{LaB}_6$ . At  $1500^\circ\text{C}$ , for example, the average lifetime of a lanthanum atom on the  $\text{LaB}_6$  surface is five minutes, while the average replacement time of this atom is only six seconds. At temperatures below approximately  $1890^\circ\text{C}$ , the evaporation rate is determined by the surface energy of the lanthanum on the  $\text{LaB}_6$ ; and for temperatures above this, it is determined by the rate of diffusion of the lanthanum atoms to the surface. At current densities above 70 amperes per square centimeter, the current should increase at a rate less than that given by Eq. (1) because of lanthanum depletion on the  $\text{LaB}_6$  surface.

The emission from the alkaline-earth borides appears to decrease with time when operated at high temperatures. It is believed that this is caused by inadequate diffusion rates of the alkaline-earth metals through the

boron framework, although this was not thoroughly investigated. This seemed to be especially true for  $\text{CaB}_6$  since a residue (consisting probably of boron) was always found on the surface after it had been operated in vacuum at high temperatures.

As would be expected from the metallic character of the boride cathodes, the pulsed emission does not differ from the steady dc emission. Figure 15 shows a Schottky plot of the emission obtained from a  $\text{CeB}_6$  cathode. The cathode consisted of a sintered rod ground to 0.184 inch in diameter and 0.430 inch long. This was heated by the anode which consisted of a tungsten coil 0.308 inch inside diameter and 0.750 inch long. The points on this curve for field strengths below 20 kv/cm were obtained with a dc anode voltage. The points for field strengths greater than this value were obtained with 5-microsecond pulses at a 60-cycle repetition rate. It can be seen that as the electric field increases up to approximately 300 kv/cm, the slope of the curve decreases approaching the Schottky value. For fields greater than this, the slope of the curve again increases. The cause of this is uncertain. It may be field emission effects or possibly very fine scale patchiness.

Many of the  $\text{LaB}_6$  properties already discussed have been confirmed by photoelectric measurements. A  $\text{LaB}_6$  photo-cell was constructed as follows. A graphite cylinder was coated with  $\text{LaB}_6$ . Provisions were made for heating this cathode by radiation from a tungsten coil within. A cylindrical molybdenum anode surrounded the cathode and contained a small opening in the side for admitting the light. Corning 9741 ultra-violet glass was used in the cell envelope. The  $\text{LaB}_6$  was sintered on the graphite at  $1800^\circ\text{C}$  and the anode was outgassed by electron bombardment from the cathode. Tungsten and barium getters as well as an

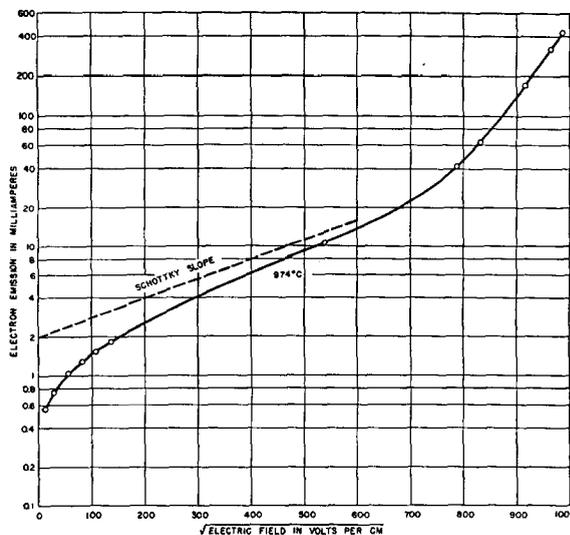


Fig. 15. A Schottky plot of the electron emission from cerium boride.

ionization gauge were sealed in appendages on the photo-cell. The vacuum was better than  $10^{-7}$  mm of Hg after sealing off. The cathode was then flashed at  $1200^{\circ}\text{C}$  before taking data.

The spectral distribution of the photoelectric yield in electrons per quantum from  $\text{LaB}_6$  at room temperature is shown in Fig. 16.<sup>10</sup> This curve is parabolic, characteristic of a metal, over at least a 0.75-electron volt range. The work function determined from this curve by Fowler's method is 2.67 volts. This in excellent agreement with 2.66 volts determined thermionically and indicates that the work function is not appreciably temperature dependent. This conclusion was checked further by varying the photo-cathode temperature from  $300^{\circ}\text{K}$  to  $700^{\circ}\text{K}$  and observing that the photoelectric yield and work function did not change.

Explorations made over the surface of the  $\text{LaB}_6$  showed some large scale patchiness with the work function increasing by not more than 0.1 volt. Increasing the anode voltage from 10 volts to 200 volts caused the emission to increase 30 percent at the 3.39-electron volt point, indicating small scale patchiness. This is also evident for  $\text{CeB}_6$  in Fig. 15 by the large slope of the Schottky curve at low fields.

#### VIII. ACKNOWLEDGMENTS

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<sup>10</sup> The writer is indebted to Dr. L. Apker and Mr. E. Taft of this laboratory for the photoelectric data presented in this paper.

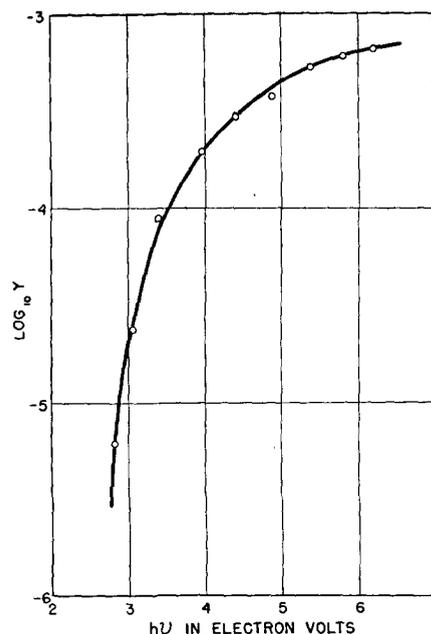


FIG. 16. Spectral distribution of the photoelectric yield in electrons per quantum from  $\text{LaB}_6$  at  $300^{\circ}\text{K}$ . The work function determined by Fowler's method from this curve is 2.67 volts.

ing and sintering the boride samples. Dr. D. Harker and his group identified many of the pure borides and solid solutions of mixed borides by x-ray analysis. Dr. H. Liebhafsky and Mr. L. B. Bronk made chemical analysis on some of the samples, and Mrs. A. P. O'Hara made spectrographic analyses of the materials used and of many of the boride products. The writer is also very grateful to Mr. C. Bell for his valuable help in preparing cathodes and expediting tube construction.