formation of electrodes and sample takes place, the disturbances die down, and at last a reproducible highest breakdown value is reached, with the characteristics of a central breakdown. The formation once achieved seems to be permanent, because if a sample is treated in the way described and the voltage just before the expected breakdown value is cut down and after some time raised again very rapidly, the final high value results. It is hoped that a more detailed study of the current phenomena will give an understanding of this new effect. Until then the values published should be taken as preliminary results.

Simultaneously with our abstract for the Washington meeting a letter of Austin and Hackett appeared in Nature[25] reporting the breakdown strength of KBr as a function of temperature. The general shape of the curve given is in good agreement with our results. The absolute values lie lower than ours at the lower temperature end of the characteristic and have not been followed up above 350°K.

Some of the crystal samples used were kindly furnished by Professor D. C. Stockbarger, to whom the authors wish to express their gratitude.

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[25] A. E. W. Austin and W. Hackett, Nature **143**, 637 (1939).

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On the Thermionic and Adsorptive Properties of the Surfaces of a Tungsten Single Crystal*

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The thermionic emission from a spherical tungsten single crystal has been observed. Photographs and diagrams show qualitatively the dependence of this emission on crystallographic direction. Nearly all the maxima and minima lie on a 110 zone. Similar observations have been made on the same crystal when caesium and barium were adsorbed thereon. Adsorption forces are largest for caesium on surfaces of highest work function. For barium the adsorption forces appear to be more dependent on surface structure as the force between the ion and its image contributes the major part of the adsorption energy. The behavior of adsorption as a function of crystallographic direction is such that the sphere surface may be approximated by that which would be obtained by carving the sphere from a perfect lattice. There is no evidence for a faceted or step-like microstructure. Emission from the spherical crystal when caesium is adsorbing on contaminated complex surfaces is more complicated in its dependence on crystallographic direction than when the surface is clean, and a map of the emission over the crystal changes its configuration with temperature. This behavior is not observed when the surface is clean or only slightly contaminated.

Introduction

It has been realized for some time that thermionic and photoelectric emission (in an accelerating field) from a clean metal surface in good vacuum may vary by some orders of magnitude depending on which surface of the crystal is studied.[1–3] Ordinarily, polycrystalline aggregates have been used for experiment in the past, and consequently the data represent some sort of an average of the emissions from a great variety of surfaces.[4, 5] Theories thus far pro-

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[*] Part of a thesis presented for the degree of Doctor of Science from the Department of Physics, Massachusetts Institute of Technology, June, 1938.

[‡] Coffin Research Fellow, 1937–38.

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[1] C. E. Mendenhall and C. F. deVoe, Phys. Rev. **51**, 346 (1937).

[2] E. W. Muller, Zeits. f. Physik **106**, 541 (1937).

[3] R. P. Johnson and W. Shockley, Phys. Rev. **49**, 436 (1936).

[4] L. H. Germer, Phys. Rev. **25**, 795 (1925).

[5] W. B. Nottingham, Phys. Rev. **49**, 78 (1936).

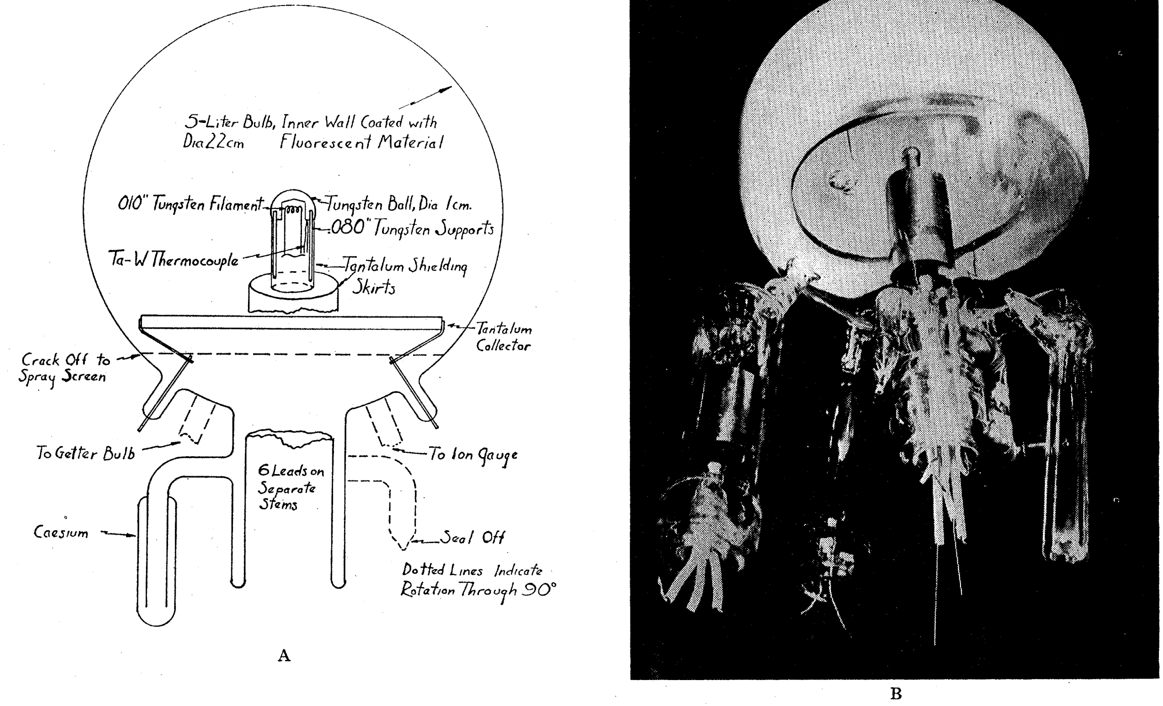

FIG. 1. Diagram and photograph of experimental tube.

posed,[6, 7] fail to consider the directional properties of the crystal structure of the emittor, as have the most precise experiments. Although an equation of the same form as the Richardson equation accurately represents the data,[5] in view of the known variation in emission from various surfaces, this is only fortuitous coincidence.

In order to proceed with further investigations, it is necessary to know which of the possible surfaces appearing on a metallic crystal are the most important in emission properties. After this information is established qualitatively, quantitative studies[8] may be made on the surfaces so selected.

Furthermore, present knowledge of the nature of the adsorbed phase of alkali and alkaline earth materials rests strongly on the work of Taylor and Langmuir,[9] Becker,[10] and deBoer and Veenemans,[11] who have determined the influence of the adsorbed metal on the thermionic emission from tungsten and nickel. It is desirable to investigate the nature of the variation in emission and adsorption over various crystal surfaces which were very likely present on their wires, as indicated by the work of Johnson and Shockley.[3] This is particularly true since the conclusions depend directly on a calculation of emission density with and without adsorbed materials. Unless a particular treatment has made the wire surface homogeneous, the average densities measured may deviate widely from those which should be considered.

One of the most provocative developments in this problem was the device of Johnson and Shockley, with which it is possible to compare visually the emissions from various parts of a single crystal filament. However, regardless of what surfaces may be developed or suppressed on such a filament, the information yielded by this apparatus can include no more than that pertaining to those directions* normal to the wire axis. Consequently from a single crystal

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[6] S. Dushman, Phys. Rev. **21**, 623 (1923).
[7] L. Nordheim, Physik. Zeits. **30**, 177 (1929).
[8] M. H. Nichols, M.I.T., Doctor's Thesis, June, 1939.
[9] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).
[10] J. A. Becker, Phys. Rev. **28**, 341 (1926).
[11] J. H. deBoer and C. F. Veenemans, Physica **1**, 953 (1934).

* A crystallographic direction is defined by the unit vector normal to a crystallographic plane. Each is designated by the same Miller indices.

wire, only information about a single zone† is obtained.

Shockley recognized that it might be possible to obtain a qualitative map of the emission properties of all the surfaces of a crystal, by using an apparatus similar to that employed[3] previously except that the cathode would be a sphere instead of a cylinder, and corresponding changes made in the rest of the geometry of the tube. He constructed such an apparatus while at Massachusetts Institute of Technology but because of a limitation of time and an unsatisfactory etching treatment of the cathode, no significant results were obtained.

In this apparatus a spherical crystal was placed concentrically in a bulb whose inner wall was coated with a fluorescent material. When the sphere was heated and a strong accelerating field for electrons applied, these proceeded radially from the sphere to the bulb. Bright regions on the bulb were then in one to one correspondence with emission regions on the sphere. Because of the necessarily large size of cathode, magnification was not great. However, providing the surfaces developed on the spherical crystal were characteristic of the crystallographic directions normal to them, this was unimportant.

APPARATUS AND PREPARATION

Apparatus

The apparatus* is shown schematically in Fig. 1A, and a photograph of the assembled tube is shown in Fig. 1B. It will be seen that the cathode was really a truncated sphere, mounted on two 0.080″ tungsten rods. A 0.25″ hole (of the same depth) in the base accommodated a 0.010″ tungsten filament of $6\frac{1}{2}$ turns, capable of giving an emission of about 0.5 ampere. This was insulated from the sphere and the high temperatures necessary for cleaning the sphere surface obtained by drawing emission from this filament to the sphere at about 1400 volts. (At 2800°K the sphere radiated about 500 watts.) A large tantalum strip circle served as collector for emission electrons from the sphere. When a voltage of about 5000 to 10,000 volts was applied between sphere and collector, electrons from the sphere surface went radially to the fluorescent screen and secondaries from this established conduction to the collector.[12, 13]

Other accessories shown in the diagram and photograph are the tantalum shielding skirts which suppressed unwanted electrons from the heating filament, and prevented field emission electrons from welds in the supporting structure, from reaching the screen. In some cases the edges of the outermost skirt also contributed field electrons, so that this was only partially successful. Also indicated are side bulbs with barium getter, ionization gauge, and caesium trap.

Preparation of the sphere

Lacking definite information as to how to prepare a crystalline surface representative of the direction normal to its macroscopic area, the sphere was polished by metallurgical methods, after initial machining, to produce a smooth bright finish. As viewed under a microscope, it was seen to be covered with a multitude of small pits having glassy sides.

The machining was accomplished entirely by grinding. At first a large ingot of sintered tungsten,* consisting of a few very large crystals,

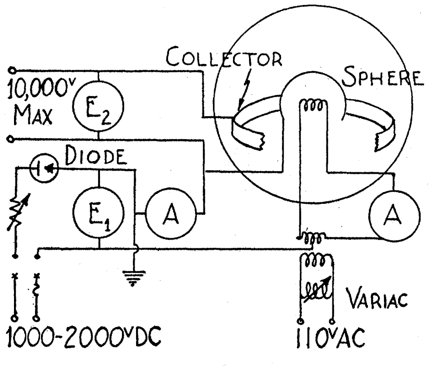

FIG. 2. Circuit diagram.

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† A zone: The set of crystallographic planes containing a common direction. Since there is a difference between a crystallographic plane and the surface (ideal) defined by the same normal, a zone is here intended to mean the set of directions lying in a common plane. Surfaces will be designated by the indices of their respective normals.

* Basically this is the same as that made by Shockley, but there are several major differences in design and construction.

[12] W. B. Nottingham, J. App. Phys. **8**, 762 (1937).

[13] S. T. Martin and L. B. Headrick, J. App. Phys. **10**, 116 (1939).

* This was kindly furnished by Dr. P. P. Tarasov of the Cleveland Wire Works, General Electric Company. It showed large cleavage surfaces when broken. Although there is some change in density when such tungsten is drawn, it is very evidently far from being porous, and shows every indication of having reached an equilibrium lattice condition.

was ground cylindrical. The three holes used for support rods and filament were drilled in the base using Carbaloy drills. The largest was used to accommodate a mandrel, the two smaller for shear pins. Tantalum strips welded to the base were used to hold the assembly together. A hand grinder mounted on a turning lathe swivel, while the mandrel rotated in the lathe chuck, produced a roughly spherical surface. This was finished with successively finer grades of carborundum and a thick-walled copper tube as tool. In this operation, the tool rotated in the lathe, the mandrel in an electric hand drill. The sphere was pressed into the end of the tube and carborundum and oil painted on. The angle between the mandrel and the grinding tool axes was varied smoothly and randomly to produce a quite accurately spherical surface. The final polish was accomplished with a rouge-charged felt in place of the copper tube.

The finished sphere measured about 1 cm in diameter and required about four or five weeks to produce. Large crystals of tungsten are brittle and will shatter if subjected to undue mechanical shock.

Preparation of the envelope

The envelope consisted of a 5-liter Pyrex bulb opened as shown in Fig. 1A, on a small circle at about latitude 40°.* The collector was welded to previously inserted stems on the neck part, and a fluorescent screen sprayed on the interior of the globe part.

Fluorescent screen

In order to get a large uniform fluorescent screen, spraying was practically imperative. The fluorescent material, a mixture of willemite and calcium tungstate, was ball-milled from 8 to 16 hours with acetone in a porcelain ball mill using flint or mullite balls. To the resulting mix, just before spraying, was added nitrocellulose binder in diatol (commercial diethyl carbonate) in the proportions of a few drops of binder per 50 cc of suspension. This binder improved the suspension markedly and also helped the screen stick to the glass when sprayed. A spray gun made from two concentric glass nozzles with material feeding through the inner one was used. It was found necessary to make a very heavy coating so that direct light from the sphere would not reach the camera when photographing the emission of clean tungsten. When this was done, and a Wratten No. C 49 filter used in conjunction with motion picture positive film, the emission pattern of clean tungsten showed fair contrast, although there was a background of about 250 watts of continuous radiation at 2100°K from the sphere, only ten centimeters away from the fluorescent screen.

Protection of the fluorescent screen

It was found that caesium vapor not only destroyed the luminescence of the material, after a few hours, but had the effect of loosening it from the bulb wall. Under the action of high velocity electrons, the material acted as though charged positively and would flock back to the cathode. In an early tube, the entire screen left the bulb wall and coated the sphere with a hard eggshell-like coating.

To prevent this, the screen was treated with a 5-percent solution of pure potassium silicate. First the binder was burned out by baking in air to 550°C, then the potassium silicate was gently washed over the inside of the bulb. This was dried while rotating in an inverted position to assure a uniform coating (rather slight non-uniformities in this coating produce bothersome dark streaks and patches in the patterns). After wiping the crack, and its neighborhood, free of the silicate (otherwise the sealing properties of the glass are seriously affected), it was again baked to 550°C in air. Following this the screen was well washed with distilled water (much sloshing) to clean out poorly anchored particles, and the process repeated. When so treated the tube required an appreciably longer time for proper exhaust but no trouble was experienced with poorly anchored particles accumulating and decomposing on the hot sphere.

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* The large size (7″ diameter) and inconvenient placement of this crack-off make the following a most effective procedure. A short section of the desired crack was scratched with a glass-knife. The scratch was heated with a hot iron, then wiped with a damp rag to start the crack, which tended to run away on a great circle of the globe if the iron was too hot. The crack was then led around the desired path with the hot tool. I am greatly indebted to Mr. Lawrence Ryan, assistant glassblower, for this effective technique.

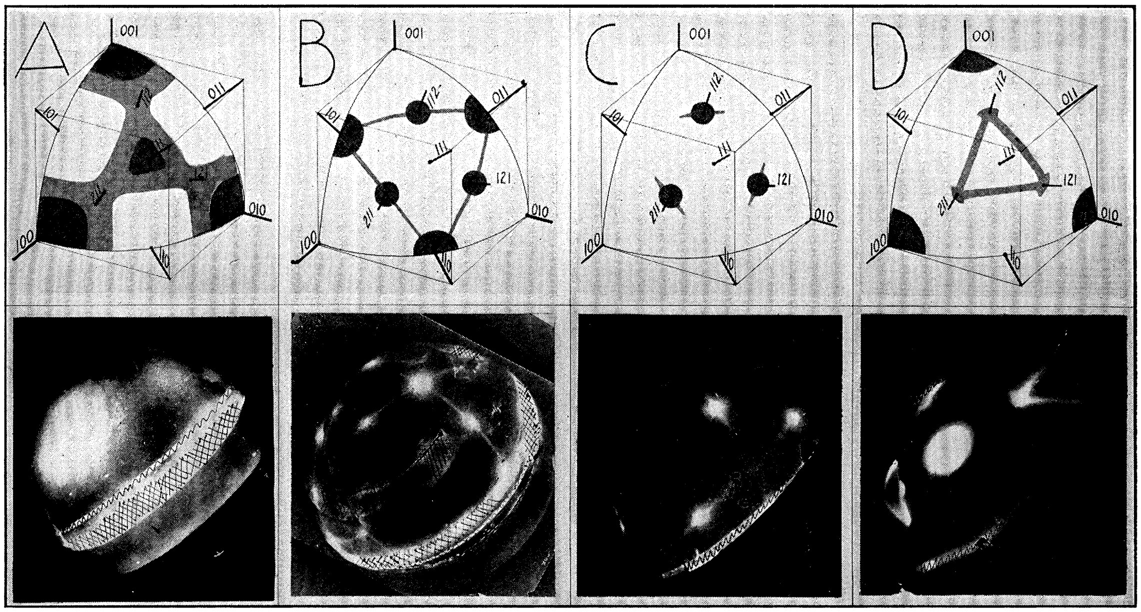

FIG. 3. A. Emission pattern of clean tungsten. B. Emission pattern of caesium on clean tungsten. Temperature range about 200°K. C. Emission pattern of caesium on slightly contaminated tungsten. Same temperature range as B. D. Emission pattern of barium on tungsten.

Exhaust

The two parts were resealed and the blank given a preliminary exhaust with baking to 500°C and the collector cleaned by high frequency treatment. After assembling the tube it was exhausted for 60 to 70 hours with baking at 500°–510°C (trap and connecting tubing baked simultaneously) on a system which had a computed speed at the tube seal-off, of 15 liters/sec. At the end of this time the pressure was of the order of 10^{-7} mm of Hg with the ovens at full temperature.

Inasmuch as all metal parts were tantalum or tungsten, and alignment was not very critical, they were outgassed at 1600°–1800°K for about an hour per part (including ionization gauge), and the sphere run at 2600–2800°K for several minutes. An emission current of 15–20 ma at 6000–8000 volts (about the limiting potential of the phosphor) was drawn to the screen for 30 minutes to further outgas this. After flashing the barium aluminum getter (tantalum clad) the tube was sealed off from the pumps with the usual precautions.

Pressure measurement

A constant check was kept on the pressure in the sealed-off tube. The tantalum and tungsten ionization gauge, when used in conjunction with a 10^{-10} amp./mm galvanometer, had a calibration such that a deflection of 2 mm on the scale with an electron current of 20 ma, corresponded to a pressure of 5×10^{-9} mm of Hg. After the exhaust procedure outlined above, this was the recorded pressure in the tube No. 3, results from which are taken to represent caesium on clean tungsten. The ionization gauge had been checked for Barkhausen oscillations and photoelectric current from the plate.

RESULTS

Method of observation

At the temperatures at which clean tungsten emits sufficiently for this type of observation (2100°K), it was found that the sphere radiated enough power back to the heating filament to cause the circuit resistance to decrease with increasing power input. A diode, with tungsten filament operating on the knee of its *i vs. V* curve, in series with the sphere heating circuit, corrected this destructive tendency. The desired maximum current was fixed by adjusting the current in the diode filament, while manipulation of a load resistor and the generator voltage

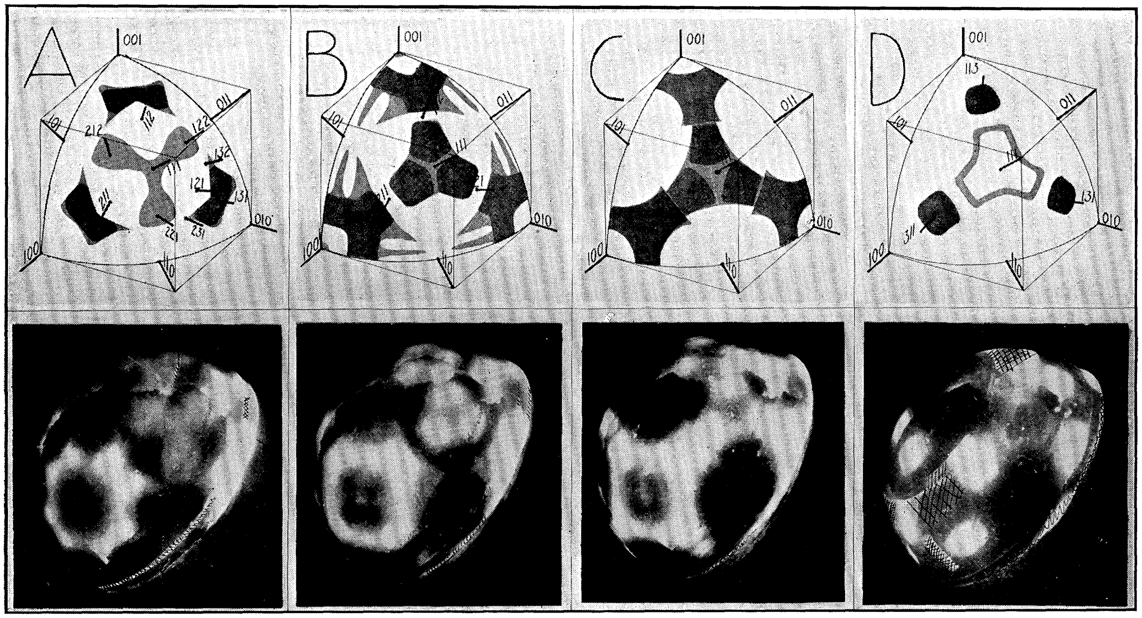

Fig. 4. Emission patterns of caesium on a contaminated complex surface, from tube No. 3, before flashing but after torching trap. Temperature increases from left to right. Temperature range about 300°K. Currents: A 0.20 ma; B 1.2 ma; C 0.85 ma; D 0.09 ma.

controlled the power input. Circuit diagram is shown in Fig. 2.

To observe the emission pattern of clean tungsten, the diode filament current was adjusted according to a previous calibration, then E_1 increased, and simultaneously the current in the sphere heating filament increased slowly until the sphere came up to its desired temperature. It was necessary to keep the emission from this filament "saturated" as this was the only convenient check on its temperature. After temperature was established, E_2 was applied and the pattern photographed.

To observe the emission pattern of caesium on tungsten, it was only necessary to remove liquid air from the caesium trap, warm this up gently, then after applying E_2, heat the sphere through the emission range for caesium activated tungsten by radiation alone from the sphere heating filament.

In the case of barium, which had to be evaporated on to the sphere from an exterior source, it was necessary to heat the sphere by electron bombardment and allow the barium to migrate and the excess to evaporate away (T about 1200°K) before a significant pattern was observed. The temperature range of emission was also somewhat above that which could be reached by radiation from the heating filament alone.

Explanation of observations

For explanation of the results it is best to refer to Fig. 4, A, B, C and D. Fig. 3 will then be discussed. Currents are not given except in this case because of large extraneous emission from the sphere mount.

In Fig. 4, the bottom row consists of photographs of the tube exterior when emission was being drawn from the sphere with caesium adsorbed on the surface (as will be discussed, there are also contaminating agents present). Four different consecutive sphere temperatures are represented, the lowest being at the left. In the top row are diagrams corresponding to the photographs below. Because the symmetry of the patterns is that of the body-centered cubic lattice,* the orientation of the underlying crystal may be determined immediately. This orientation is specified in the diagram by the outlined

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* Tungsten crystallizes in the body-centered cubic lattice, two atoms per unit cell, and so has the following elements of symmetry: three 4-fold axes, four 3-fold axes, six 2-fold axes, and nine reflection planes.

cube which represents the unit cell of the crystal. The map itself is the projection of an octant of a sphere whose center coincides with the backmost corner of the cube. Dark patches on the maps correspond to light patches on the photographs. The important crystallographic directions of each photograph are drawn in the diagrams as short black lines emerging from the surface of the octant. They are labeled with their Miller indices.

The diagrams appear to have more symmetry about the threefold axis than the photographs because the pattern of a neighboring crystal grain with somewhat different orientation appears in the upper part of each photograph. Since only an octant is drawn in the diagrams, the fourfold symmetry of the photographs is suppressed. Despite the fact that the whole sphere is not one single crystal, all the information that could be gained from one is to be found in the triangle defined by the 100, 110 and 111 directions. This triangle is repeated forty-eight times on a perfect spherical single crystal. The diagrams are drawn as though they were part of such a single crystal.

These patterns from a contaminated surface show the various symmetry axes so well that they are useful to fix the orientation of the crystal. Subsequent photographs are from nearly the same angle so that the various directions may be identified even though the patterns show much less detail. In general the orientation is much easier to see in the pattern on the bulb itself than in the photographs of it.

Clean tungsten

Figure 3, A shows the emission pattern from clean tungsten (no adsorbent) at a temperature of about 2100°K. Emission is strongest from a large region around the 100 direction (but the 100 itself is somewhat weaker), next strongest around the 111 direction. The 211 is the next most important, and the 110 the poorest emittor. Surfaces ranked in order of decreasing work function are thus 110, 211, 111 and the group neighboring on the 100. Qualitatively this agrees with the results of Mendenhall and deVoe,[1] who found the 310 to have a lower photoelectric work function than the 211 surface, and the pattern is similar to some published by E. W. Muller[2] representing the field emission from a single crystal tungsten point. Except for some of the emission from the region around the 100 direction, all the maxima and minima lie on a 110 zone. This is fortuitous for quantitative thermionic studies as a drawn wire, recrystallized by slow heating in hydrogen to form large single crystals, contains this direction in the wire axis.[14]

Crosshatched regions on the photographs indicate spurious emission, either from electrons coming from the interior heating filament through a crack in the shielding skirt, or from field electrons drawn either from the edge of the base of the sphere, or from edges of the shielding skirts, or other points on the cathode support not sufficiently shielded.

Caesium on clean tungsten

Figure 3, B shows the emission pattern when caesium is adsorbing on the clean sphere surface. Reference to the map shows that emission occurs from small regions at the 211 direction and somewhat larger ones at the 110 directions, and also along very narrow lines connecting these spots. These lines are zones whose axes are the 111 directions. (A set of directions will be specified by that one of the set whose indices are all positive and in order of decreasing magnitude.)

A very important feature of this observation is that the configuration of the pattern remains unchanged throughout the observable range of emission. Certain unfortunate accidents prevented measurement of the temperatures in this range, by means of a tantalum-tungsten thermocouple designed for this purpose. Extrapolation of a power input *versus* temperature curve established from 1100°K upwards shows the temperature range to be at least 200°K.

This pattern occurred in the third and best caesium tube constructed. Once it had been established by flashing the sphere to 2600–2800°K it did not change its configuration on subsequent flashings, and further, remained stable for a period of three hundred hours without intervening flashings or other treatment.

Caesium on slightly contaminated tungsten

Figure 3, C is the emission pattern obtained immediately after flashing the sphere, and allow-

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[14] R. B. Nelson, M.I.T., Doctor's Thesis, June, 1938.

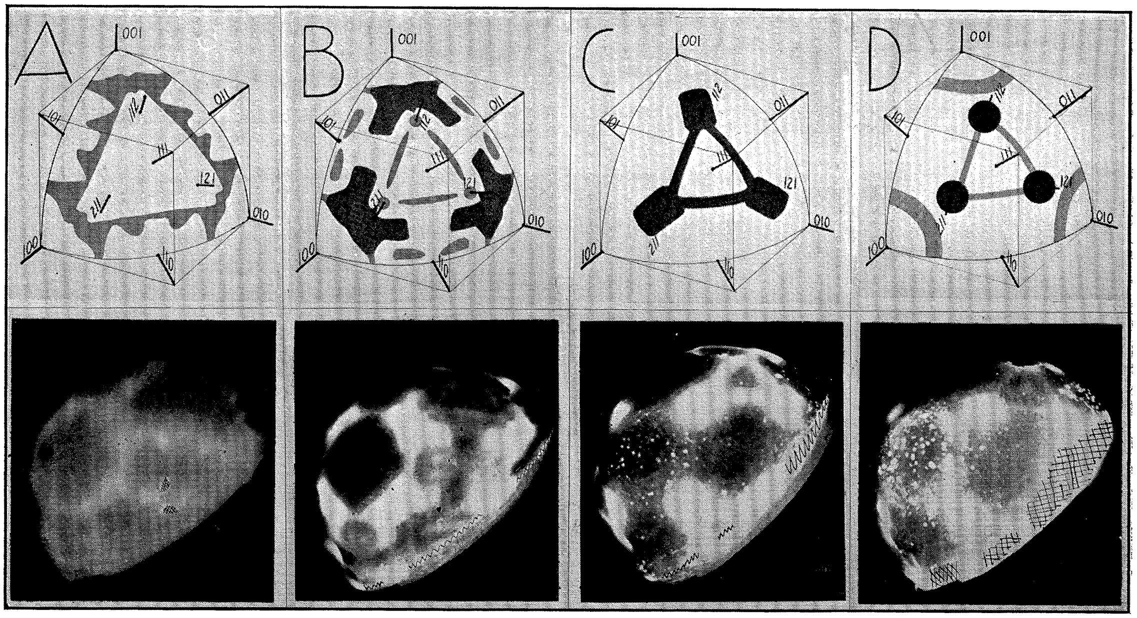

FIG. 5. Emission patterns of caesium on a contaminated complex surface, from tube No. 2, before flashing but after torching trap. Temperature increases from left to right. Temperature range about 300°K.

ing caesium to adsorb on it, in the *second* caesium tube constructed. The *very* extreme precautions used in the construction of the third tube were not exercised, although baking and outgassing were quite comparable. The configuration of this pattern was also invariant to temperature change, but under certain conditions other patterns would appear after a period of 24 hours (see Fig. 6). The two patterns are the same except that the emission from the 110 spots is suppressed as is also part of the 111 zones.

Barium on tungsten

The emission pattern from barium is shown in Fig. 3, D, after the barium had migrated to an equilibrium configuration. Contrary to evidence presented by Benjamin[15] no particular difficulty was experienced in getting the barium to migrate, although it takes some time as the distances involved are much larger than those normally encountered. Immediately after evaporation of barium on the sphere,* emission was observed to come from all portions of the sphere exposed to the source, and this emission was not related to the underlying crystal.

Successive observations were made as barium was evaporated. This was the only pattern having a symmetrical nature which was observed. After the pattern was established, there was no change in configuration on further evaporation until the emission was too small for further observation.

The important directions are indicated by the roundish patch at the 100 direction, and the triangle whose corners fall at the 211 directions. This triangle shows again in one of the patterns from caesium on a contaminated surface (Fig. 5, C). Ahearn and Becker[16] have found that thorium migrates preferentially along a 111 direction on a 211 surface. This direction would bisect the angles of the triangle.

The 100 direction spot was much stronger in emission than the rest of the pattern, held the

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[15] M. Benjamin and R. O. Jenkins, Phil. Mag. **26**, 1049 (1938).

* This source of barium was developed by Dr. E. A. Lederer of the RCA Manufacturing Company, Radiotron Division, Harrison, New Jersey, and kindly loaned by Dr. G. R. Shaw. A double oxide of barium and beryllium is reduced by heating on a tantalum strip. Barium deposits so made are clean and bright. If used carefully, the ionization gauge shows a change of pressure of less than 10^{-9} mm of Hg when the process is started and stopped, provided it has been well outgassed. However, the presence of thermionically important quantities of oxygen or oxide in the deposit is not entirely ruled out.

[16] A. J. Ahearn and J. A. Becker, Phys. Rev. **54**, 448 (1938).

barium at higher temperatures, and when the pattern was first established, before too much evaporation had taken place, was visibly affected by the applied field.

Caesium on contaminated complex surfaces

The patterns of Fig. 4 (obtained in the third caesium tube before flashing) are emission patterns from caesium on contaminated complex surfaces. The contamination arises from gases released in the caesium trap by gentle torching necessary to drive caesium into the bulb proper. As the temperature increased the configuration changed gradually, and these are representative examples. The total emission passed through a maximum as the temperature was increased. Provided the temperature was not raised too high (roughly 1200°K) the same configurations appeared whether the temperature was increasing or decreasing. After flashing only the pattern of Fig. 3, B appeared.

Figures 5 and 6 represent observations made on the second caesium tube constructed. In Fig. 5 the caesium trap has been gently torched just before the observation. The observation of Fig. 6 is one of several made a few days later and represents an accumulation of contamination following flashing of the sphere to 2600°–2800°K after the observation of Fig. 5.

Nature of contamination

Both of these tubes were gettered with barium which is known to be effective for all manner of common gases. The long bake at high temperature seems to make the presence of water vapor unlikely but aside from these almost any other gas likely to remain in the Pyrex or in the caesium, the outgassing of which had received a great deal of attention, is a possibility for Figs. 4 and 5.

Dissociation of particles of screen material which have found their way back to the cathode is the most probable source of the contamination occurring in Fig. 6. This is one of many sets of observations made over a period of several days. With this and the preceding tube about twenty different sets of these observations were made by allowing the sphere to remain at about 1200°K overnight and taking the observations on successive days. Patterns were never duplicated. Some were of amazing complexity but all displayed the required symmetry. After a sufficient time a pattern having no discernible symmetry would occur indicating that the contamination

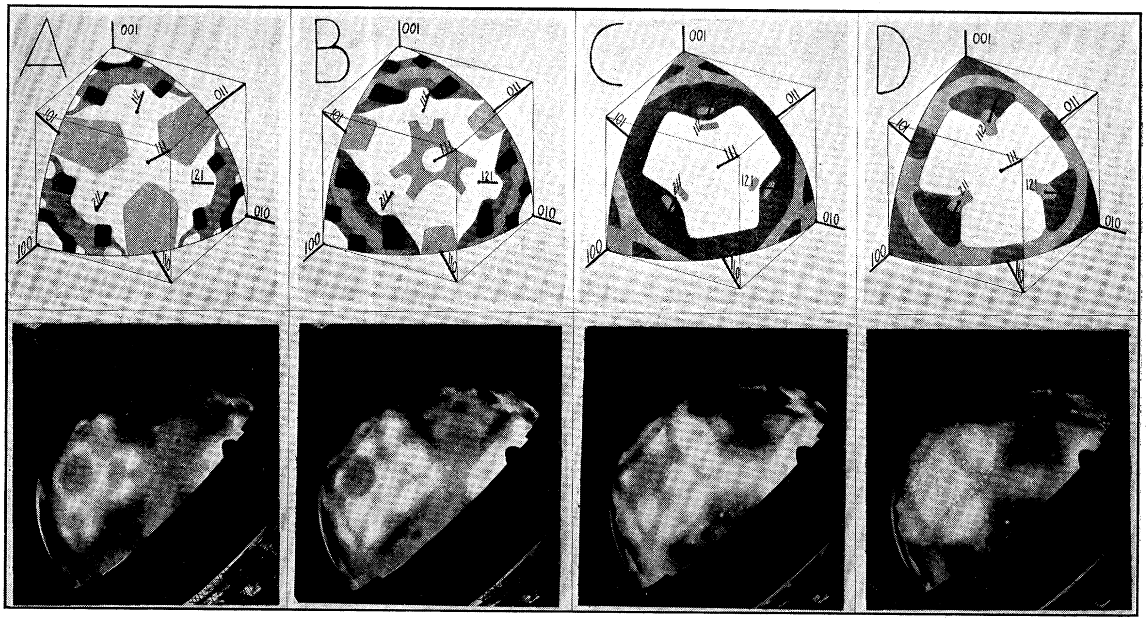

FIG. 6. Emission patterns of caesium on a contaminated complex surface from tube No. 2. This represents a moderate stage of contamination, probably by dissociation of particles of luminescent material drawn to the sphere. Temperature increases from left to right. Temperature range unknown.

had accumulated to an extent which obscured the effect of the underlying lattice. Flashing the sphere at this point invariably produced the pattern of Fig. 3, C.

Although only one crystal grain is shown in these photographs it was also observed that equivalent directions on other crystal grains on the side of the sphere away from the camera had apparently completely equivalent properties. Thus the contamination was not localized nor do the surface properties depend on the particular crystal selected.

A close inspection of Figs. 4, 5 and 6 will show that the patterns grow into one another in complicated ways as the temperature is varied. It will also show that some regions, at a given contamination, may have a comparatively low emission throughout activation, others a comparatively high emission. All that emit visibly exhibit a maximum with temperature increase, but the temperature of the maximum varies with the condition of contamination and the surface. No surface was observed to have a minimum of emission with temperature increase (over the temperature range of caesium activation).

Because the ionization gauge never showed a pressure greater than 10^{-7} mm of Hg at any time (pressure increases during flashing of sphere) after this tube (caesium No. 2) was sealed off, and generally registered a vacuum of the order of 10^{-8} (exclusive of caesium vapor), these figures are particularly interesting in showing the enormous effects of very minute amounts of gas or other contamination on adsorption studies.

X-ray orientation

A Laue back-reflection picture[17] made with the x-ray beam normal to the sphere surface at the point determined by the center of the triangular pattern of Fig. 5, C unequivocably established this as the 111. The complete check between electronic and x-ray pattern justifies the assumption that electrons go radially to the fluorescent wall of the bulb.

Discussion

Nature of surfaces

Because of (1) the symmetry of the contaminated patterns, (2) the equivalence of emission from spots on the same or different crystals having the same or equivalent directions, and (3) the fact that under different conditions of contamination, different directions having very high Miller indices show properties distinct from those of nearby regions, it appears that the surfaces developed on the sphere are completely characterized by the crystallographic directions normal to the macroscopic surface of the sphere. No one surface can be said to dominate a very large fraction of the total area.

This latter point is borne out by the observation that the boundaries of the emission regions displayed on contaminated complex surfaces moved smoothly as the temperature was raised and lowered. That is, in general no one region gained or lost emission as a whole. Instead there was a gradual encroachment of an emitting area into a nonemitting one, or vice versa. Thus the considerable high temperature treatment for good outgassing in several tubes has not produced a polyhedron which approximated to the original sphere.

There remain two alternatives. (1) A given surface may have a faceted fine structure,[18] the facets being fundamental surfaces of simple structure. Such surfaces appear on metal crystals when etched with certain reagents. If more than one fundamental facet was produced, the relative area of each kind on a given surface would be a function of the direction normal to it. (2) A given surface may be approximated by that produced when all atoms are retained whose centers lie on one side of a plane passed through the crystal. This is termed an ideal surface.

If the first hypothesis were true, then the emission properties should change smoothly and monotonically in going from the normal which specified one of the fundamental surfaces to the other. Unless one is willing to accept very complicated surfaces as the fundamental ones, Fig. 5, B and Fig. 6, A and B, cannot be explained on this hypothesis. For instance, the small bright spots of Fig. 5, B near the 110

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[17] Alden B. Greninger, American Institute of Mining and Metallurgical Engineers, Institute of Metals Division **117** (1935).

[18] L. Tonks, Phys. Rev. **38**, 1030 (1931).

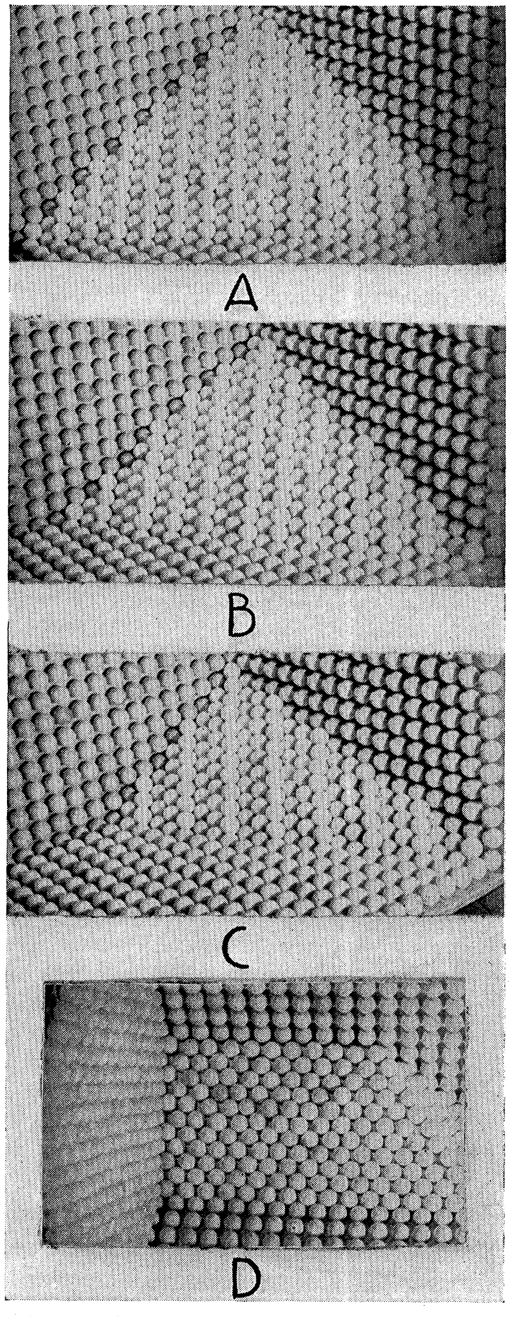

FIG. 7. Sample surfaces of $\bar{1}\bar{1}1$ zone. (*A*) 211; (*B*) 437; (*C*) 213; (*D*) 101. Floor and sides of model are 100 surfaces, except that underlying atoms are missing.

direction have indices approximately 12,9,2. Furthermore, the 110 surface has been proposed as one such fundamental facet for tungsten after high temperature treatment because of an early experiment of Langmuir's,[19] and because its high surface density of atoms and simple structure make it an appealing one. In this case it would certainly be expected that the sphere would show a step structure in a considerable region around the 110 direction with the tops of the steps consisting of 110 surfaces. The extraordinarily sharp variation of properties in this region shown in Fig. 5, B make this an unfavorable supposition. It is quite possible that Langmuir's result may be explained by etching of the surface, possibly by water vapor.

Alternative (2) is supported quite strongly by the above phenomena, and also by the fact that the line of emission extending between the 211 and 110 surfaces of the sphere in Fig. 3, B can be explained on this basis. Fig. 7, A, B, C and D, shows photographs of models of the ideal surfaces of the b.c.c. lattice whose normals are, respectively, the 112, 437, 213, and 101 directions.* These are sample surfaces of the $\bar{1}\bar{1}1$ zone.

The 211 surface consists of rows of atoms, at two different levels, forming long troughs and ridges. The 110 is a "flat" surface in that all atoms exposed are at the same level. The other surfaces of the 111 zone lying between these show a combination of these two types of structure and no other. Consequently it may be assumed that a structure sensitive property like adsorption should vary smoothly in going from the one surface to the other along this zone. If both of these give good emission under caesium adsorption, the intervening surfaces should do likewise. A tendency for this zone to behave as a unit can also be seen in Fig. 4. A similar tendency has been noted in other observations of caesium on contaminated tungsten although the cleancut behavior of uncontaminated surfaces is not expected.

Differences in caesium and barium adsorption

Caesium.—Caesium adsorbs most strongly on surfaces of highest work function (best emitting surfaces at the highest temperatures of activation are considered to have the strongest adsorp-

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[19] I. Langmuir, Phys. Rev. 22, 374 (1923).

* In making this model advantage was taken of the fact that if spheres of diameter "*a*" are pegged out on a flat surface at the corners of a square grid whose distance of repetition is $(2/\sqrt{3})a$, subsequent spheres of this diameter laid thereon automatically build up a body-centered cubic lattice.

tion forces) when the tungsten surface is clean, although there is not an exact reversal of the clean tungsten pattern. This behavior is expected since the ionization energy of Cs^+ is 3.88 electron volts. This is lower than the work function of any tungsten surface[8] and the radius of the ion is so large (2.62A for coordination number 8)[20] that variations in the energy term arising from a varying image force on different surfaces may be neglected. The determining factor in the energy of adsorption is the difference between the ionization energy of the atom and the work function of the surface.

As mentioned before the invariance of configuration of the emission pattern of caesium on clean tungsten distinguishes it from that of caesium on a contaminated surface. It is generally accepted that the work function of a homogeneous surface must have a minimum with increasing concentration of adsorbed material. Consequently a "reversal" of the emission pattern was expected as the temperature was decreased, caused by the work function of poorly adsorbing surfaces reaching a minimum at a lower temperature than that corresponding to the minimum of the better adsorbing surfaces. Such behavior is noticeable in Figs. 4, 5 and 6.

It is quite possible that the expected reversal takes place at temperatures where emission from all surfaces is below the minimum observable. This minimum current density is computed to be about 10^{-6} amp./cm^2. From previous work it is estimated that the minimum observable current density at the fluorescent screen is 10^{-8} amp./cm^2 at the voltages of operation (8000v). Linear magnification is about 20. At a room temperature of 27°C, it may be computed from the data of Taylor and Langmuir[9] that this allows observation over a "coverage" range from $\theta = 0.3$ to $\theta = 0.7$.

Barium.—DeBoer has shown[11] that the adsorption of barium is possible (he considers only electrostatic binding forces for the ions, van der Waal's forces for the atom) only if the doubly charged ion is held to the tungsten surface by virtue of the image force, since the difference between work function and ionization energy is positive and energy must be supplied to the combination metal plus ion. This energy is more than supplied by polarization of the metal by the approaching ion if the radius of the ion is sufficiently small. This is not the case when the singly charged ion is used, but in spite of the great increase in energy needed to ionize the barium atom doubly, it is true in this case because of the smaller ionic radius. Computations were made for a plane surface.

Examination of models of surfaces in the neighborhood of the 100 show that these have a large percentage of their area occupied by groups of four neighboring atoms (refer to Fig. 7 for representations of ideal 100 surfaces) so that their adsorption properties should be similar to the 100. The radius of the doubly charged barium atom must be considerably smaller than that of singly charged caesium, so that the very strong emission from this region may be accounted for by supposing that the barium is adsorbed in these places. In such a position it is effectively in a small recess in the surface and the ion and its image are appreciably closer than they would be on any other surface, resulting in a larger image force.

Since the barium pattern of Fig. 3, D remains unchanged even after a considerable evaporation of barium has taken place (total emission declines steadily), the regions from which emission is occurring may be taken as those for which adsorption forces are the greatest. The triangular emission region is not easily explained with the model. The lines are portions of 311 zones, but the surfaces of these zones do not display the regularity of the 111 zone surfaces. It has not yet been discovered why only a portion of these zones display singular emission properties.

Clean tungsten.—The emission from clean tungsten did not show the spectacular variations with direction displayed by the others because (1) it is very likely not nearly so sensitive to change in configuration of the surface as is adsorption, (2) the high temperature of observation probably makes the surfaces more nearly alike because of thermal commotion of the surface atoms, and (3) the ratio of the emissions from two different surfaces are governed by terms of the form exp $(-Ve/kT)$ where V is the difference between respective work functions,

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[20] W. Hume-Rothery, *The Structure of Metals and Alloys* (Institute of Metals Monograph and Report Series No. 1, 1936).

and the higher the temperature the more nearly does this approach unity for a given V.

Observations made on a polycrystalline wire recrystallized in the course of a few seconds by the treatment normally followed in thermionic experiments, probably represent the average of the emission of the sphere. A multitude of small randomly oriented crystals is known to result from such treatment. In such an average about half of the surface contributes at least 90 percent of the total emission. Consequently it is not remarkable that the constant A in Richardson's equation has never been found to be in satisfactory agreement with experiment. There are, of course, other factors* which may cause deviations from the theoretical value, even though observations are made on a single homogeneous ideal crystal surface.

Taylor-Langmuir and Becker experiments

The quantitative work of Taylor and Langmuir,[9] and Becker[10] on caesium adsorbed on tungsten, is difficult to evaluate in the light of these experiments because it is not possible to say with certainty what surfaces dominated their wires. The Langmuir-Taylor theory, with which the Becker experiments agree, assumes that their wires had surfaces composed of 110 facets. It is doubtful if such a surface was produced by the vacuum treatment alone, as this was quite comparable to that given the cathode in this experiment. However, etching by preliminary treatment in wet hydrogen to bring the springs into a condition where they would not twist the wire, or other preliminary treatment may have done this.

It is possible to calculate from the Taylor-Langmuir paper[9] that the work function of the wires used was 4.62 ev.* This agrees with Nichol's best value of the 110 work function of 4.65 ev.[8] Consequently it seems likely that the data are representative of the 110 surface of tungsten, as supposed.

Since the work functions of all tungsten surfaces are greater than the ionization energy of caesium, the data of Taylor and Langmuir on ion and atom evaporation are quite unimpeachable whatever the state of the surface of their wires.

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* These are: A work function which varies linearly with temperature, and loss of low energy electrons by reflection at the surface potential barrier. See reference 5.

* Langmuir approximated the Richardson equation over the temperature range 600°–1000°K with one of the form $i=A_0 \exp(-b_0/kT)$ which fits the Richardson equation $i=AT^2 \exp(-b/kT)$ at the center of the temperature range in slope and magnitude. The necessary relations are easily derived as:

$$A_0=A(T^2_M)(e^2) \quad (e=\text{base of natural logarithms})$$
$$b_0/k=(b/k)+2T_M \quad (T_M=\text{center of temperature range}).$$

Taking T_M as 800°K and their value of $b_0=(4.76/300)\times(4.80\times10^{-10})$ we obtain the above.

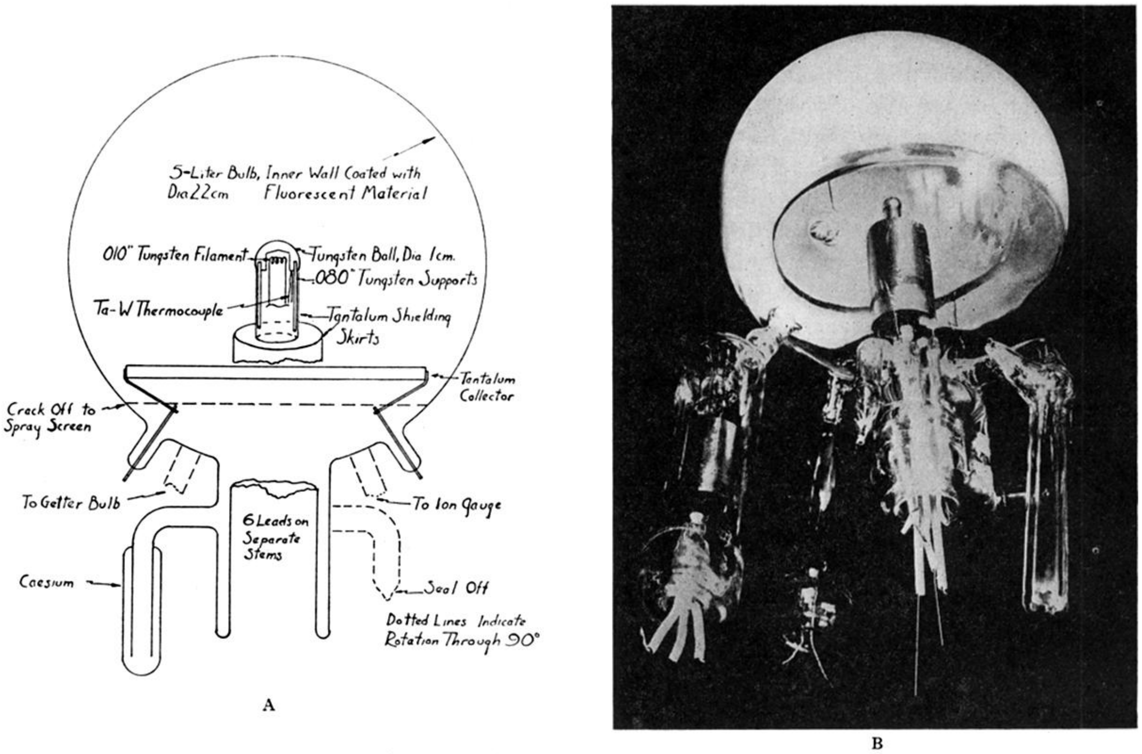

FIG. 1. Diagram and photograph of experimental tube.

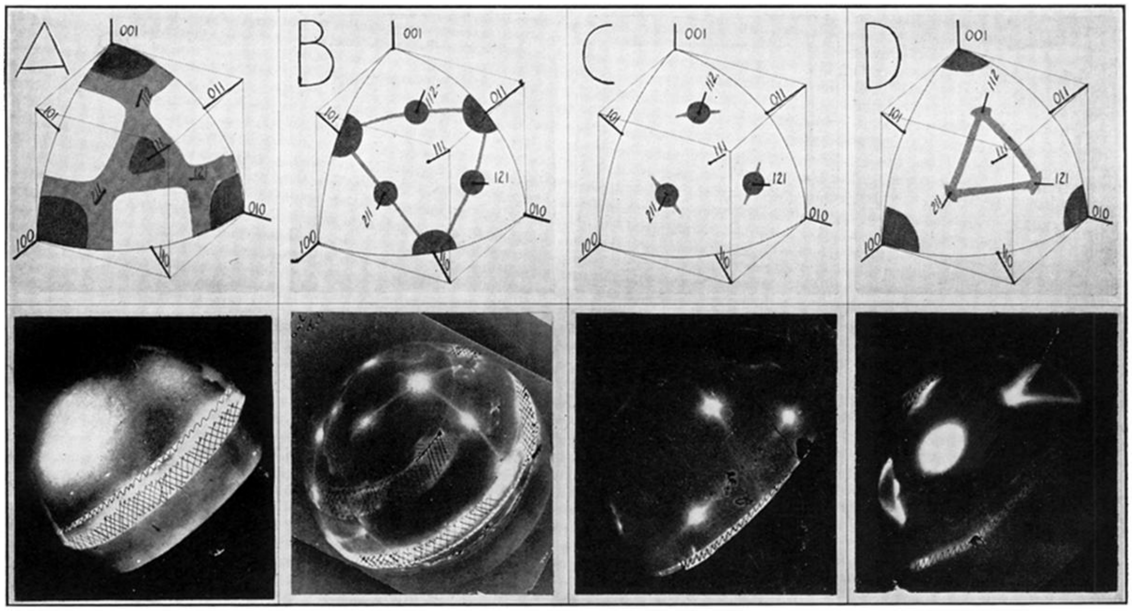

FIG. 3. A. Emission pattern of clean tungsten. B. Emission pattern of caesium on clean tungsten. Temperature range about 200°K. C. Emission pattern of caesium on slightly contaminated tungsten. Same temperature range as B. D. Emission pattern of barium on tungsten.

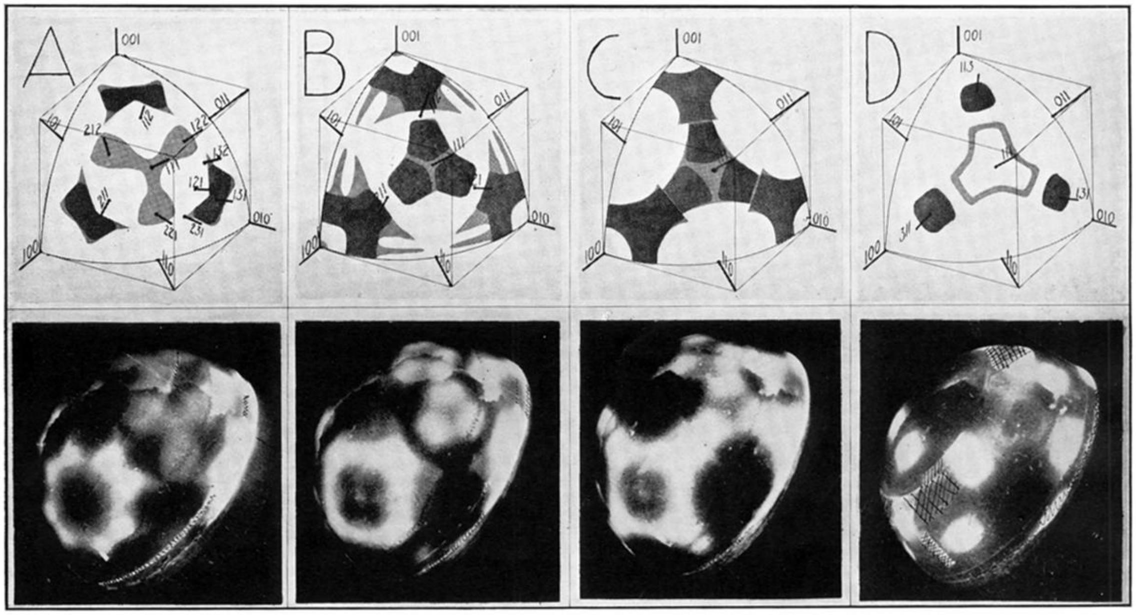

FIG. 4. Emission patterns of caesium on a contaminated complex surface, from tube No. 3, before flashing but after torching trap. Temperature increases from left to right. Temperature range about 300°K. Currents: *A* 0.20 ma; *B* 1.2 ma; *C* 0.85 ma; *D* 0.09 ma.

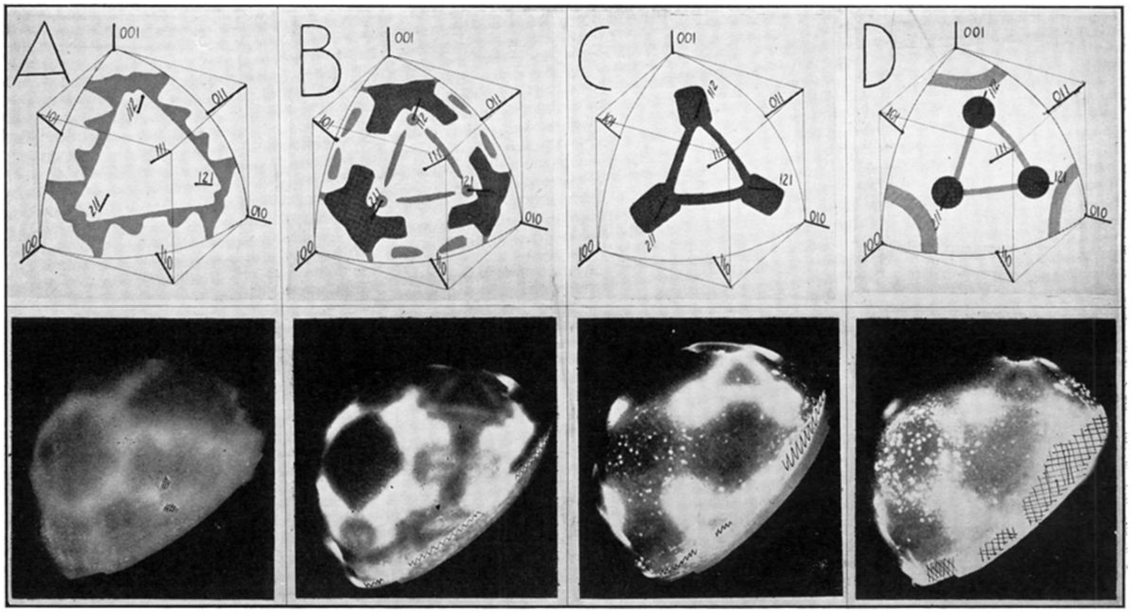

FIG. 5. Emission patterns of caesium on a contaminated complex surface, from tube No. 2, before flashing but after torching trap. Temperature increases from left to right. Temperature range about 300°K.

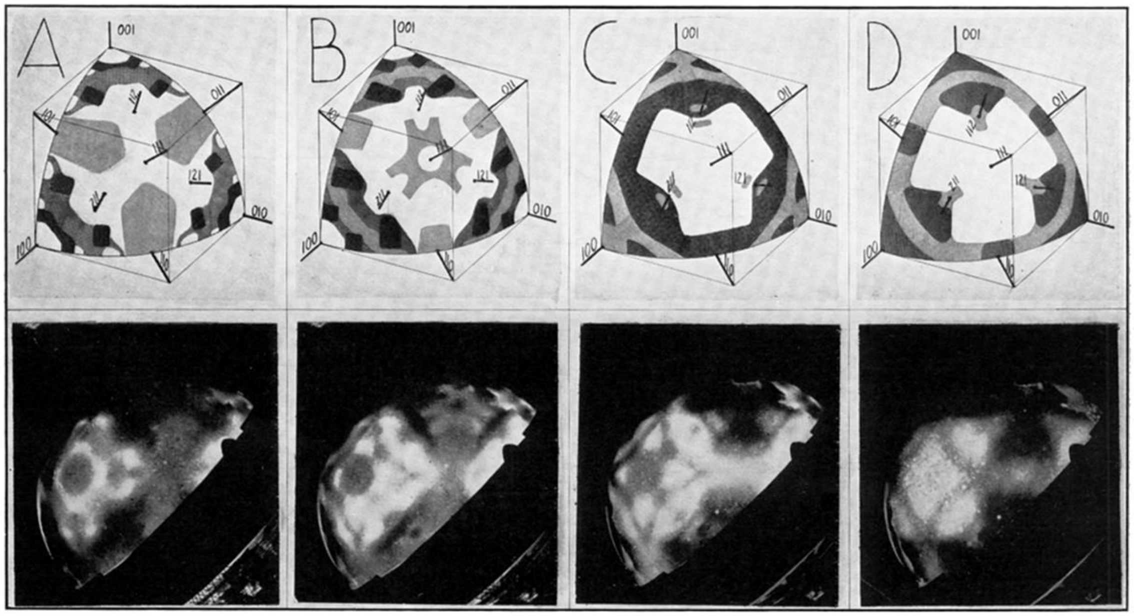

FIG. 6. Emission patterns of caesium on a contaminated complex surface from tube No. 2. This represents a moderate stage of contamination, probably by dissociation of particles of luminescent material drawn to the sphere. Temperature. increases from left to right. Temperature range unknown.

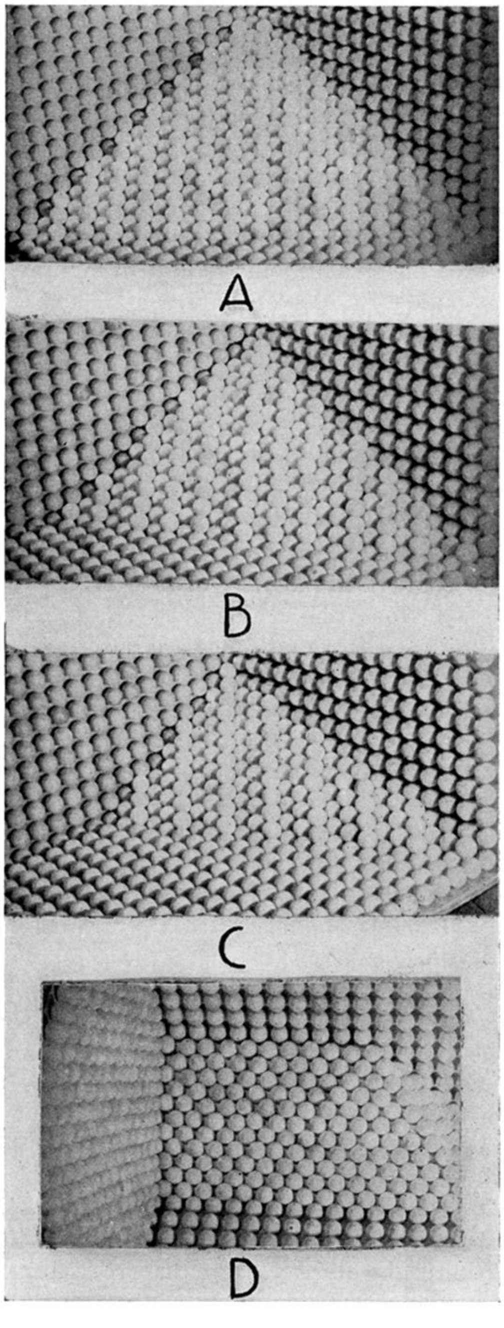

FIG. 7. Sample surfaces of $\bar{1}\bar{1}1$ zone. (*A*) 211; (*B*) 437; (*C*) 213; (*D*) 101. Floor and sides of model are 100 surfaces, except that underlying atoms are missing.