The calibration runs were taken with air in exactly the same manner, the air being dried and freed from carbon dioxide by passing through sulphuric acid, sodium hydroxide, calcium chloride, and phosphorous pentoxide. Seven such calibration runs were made, and the mean of these was used to give the ratios plotted in Fig. 3, which is a plot of the ratio of the quantity $(\epsilon - 1)$ for water vapor to that for dry air at 76 cm of mercury and 100 degrees centigrade.

Conclusions

According to the theory given by Clausius and Masotti, the quantity $(\epsilon - 1)$ should vary linearly with the density of the gas for nonpolar molecules. The results given in Fig. 3 show that this relation is also true for water vapor at constant temperature since the isothermal curves are all straight lines.

Assuming a value of 1.000425 for the dielectric

constant of air at 76 cm and 100 degrees centigrade,³ the slopes of the lines in Fig. 3 correspond to values of the dielectric constant of water vapor of 1.0071 at 76 cm and 71.9°C; 1.0060 at 76 cm and 99.8°C; 1.00475 at 76 cm and 147°C. Of these, the value at 99.8°C is the most reliable, as more points were taken to determine it. The value found by Sanger⁴ was 1+(0.600+3507/T)(density) and the present results agree with this within the limits of accuracy of the experiment.

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The author wishes to express his gratitude to Dr. S. S. Mackeown who directed the research; to Dr. I. S. Bowen for his many helpful suggestions during the progress of the investigation; and to the California Institute of Technology for the use of its research facilities.

³ H. E. Watson, Proc. Roy. Soc. A143, 558 (1934). ⁴ R. Sanger, Helv. Phys. Acta 1, 359 (1928).

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The Thermionic Constants of Tungsten as a Function of Crystallographic Direction

M. H. NICHOLS*

George Eastman Research Laboratory of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts (Received November 10, 1939)

A method is described for recrystallizing tungsten wire into long single crystals occupying the whole cross section of the wire and so oriented that one of the face diagonals is parallel to the axis of the wire. The temperature dependence of the emission associated with the different crystal directions has been investigated for one such specimen and fitted to the empirical equation $i_0 = A^*T^2 \exp(e\varphi_0/kT)$. The values of φ_0 range from 4.35 volts for the (111) crystal direction to 4.65 volts for the (110) crystal direction. The values of A^* range from 125 for the (112) and (001)

INTRODUCTION

HE work of Johnson and Shockley¹ and later of Nelson² and Martin³ has shown that the high field thermionic emission from pure and

directions to 15 for the (110) direction. A possible explanation for the low values of A^* is suggested. These results show that the values of φ_0 and A^* obtained from the usual measurements on polycrystalline wire are characteristic of a weighted average of the properties of the various crystal surfaces occurring and have, therefore, only empirical value, indicating that all attempts to relate observed to theoretical values of emission constants have so far no great significance.

caesiated tungsten surfaces depends upon the crystallographic direction normal to the emitting surface. Up to the present, all quantitative measurements of the thermionic constants of metallic surfaces have been made on polycrystalline specimens. Thus the results obtained are characteristic only of a weighted average of the properties of the various crystal faces exposed, making the interpretation of the results exceedingly complex.

^{*} Now National Research Fellow at Princeton University. ¹ R. P. Johnson and W. Schockley, Phys. Rev. 49, 439

^{(1936).} ² R. B. Nelson, M.I.T. Doctor's Thesis. (Soon to be

published.) ⁸S. T. Martin, Phys. Rev. 56, 947 (1939).

Martin's³ work with a system consisting of a small sphere, essentially a single tungsten crystal, surrounded by a concentric spherical fluorescent screen is of particular interest because it shows that of all the possible crystallographic directions normal to the surface of the sphere, the only ones possessing important characteristic thermionic properties are the (001), (110), (111), and (112) crystal directions. It has been known for some time that on account of the pure tensile



FIG. 1. Crystal growing apparatus.

stress experienced by the crystal grains near the center of a tungsten wire as it is drawn through the dies, these grains show a preferred orientation; namely, that in which one of the (110) directions coincides with the wire axis. Nelson² has shown that it is possible to recrystallize tungsten wire, polycrystalline as it comes from the dies, in such a way that crystals occupying the whole cross section of the wire are produced with this preferred orientation. This orientation makes all the crystal directions which have Miller indices of the form (hhk), which includes all the directions found to be thermionically important by Martin, normal to the surface of a smooth wire.

With Nelson's method for obtaining a properly oriented "seed" crystal, long single crystals have been produced in pure tungsten wire by a method to be described here. Quantitative thermionic measurements upon one such crystal have yielded values of the thermionic constants for the different crystal directions normal to the surface of this wire.

PRODUCTION OF SINGLE CRYSTAL WIRES RE-TAINING THE PREFERRED ORIENTATION

For a number of years single crystal tungsten wire has been produced by the firms of Julius Pintsch and others. In general, the method consists of passing a polycrystalline tungsten wire, including suitable fluxing agents, through a steep temperature gradient. This process yields single crystals, meters long, which occupy the whole cross section of the wire. Unfortunately, they contain relatively large amounts of impurity from the fluxing agent. This fact, together with the random orientation of the crystals, makes these commercial products unsuited for experimental use. The procedure set forth in the following is simply to extend a "seed" crystal, produced with the proper orientation by Nelson's method, by passing it through a steep temperature gradient.

Two Pyrex tubes A and B (of Fig. 1) of about the same diameter are mounted with interconnecting tubes C and D. The tube E leads to the vacuum system. A raw polycrystalline tungsten wire (G.E. No. 218, five-mil), having been ground and polished to remove the die marks,⁴ is mounted with suitable springs in tube A. The thin-walled glass tube F seals B from the mercury manometer and the capillary leak L. A mercury distilling apparatus is connected at K. After the tubes have been evacuated and baked, mercury is distilled in until the levels are somewhat as indicated in the drawing. The still is

⁴ R. P. Johnson, A. B. White, and R. B. Nelson, Rev. Sci. Inst. 9, 253 (1938).

then sealed off. Tank hydrogen, from which the water vapor, oxygen, and hydrocarbon vapors have been removed by passing through hot copper shot and then through a trap filled with glass beads and immersed in liquid air, is admitted through the fore vacuum end of the system until atmospheric pressure is reached. Liquid air is kept on the traps at all subsequent times. The system is flushed with hydrogen several times before the final charging.

Up to this time, the raw wire has not been heated above 1000°K, and has retained its polycrystalline nature. In order to produce a crystal seed possessing the proper orientation relative to the axis of the wire and lying just above the mercury surface in tube A, Nelson's² heat treatment process is used. The temperature of the wire is raised to 1000°K by passage of an alternating current and raised in steps of about 100° each half-hour thereafter until the temperature is about 2600°K. The presence of the hydrogen cools the surface of the hot wire so that a temperature gradient exists between the center and the surface of the wire. From a measurement of the power dissipated by a five-mil wire at 2000°K in an atmosphere of hydrogen, it has been calculated that the center of the wire is about one degree hotter than the surface. In such a small wire this slight temperature difference represents a considerable gradient which is favorable to the growth of crystals in the radial direction. Under these conditions, crystals start from parent grains near the center of the wire and grow rapidly



FIG. 2. One-dimensional electron projection tube.



FIG. 3. Photograph of the projection tube in which was mounted the single crystal wire used for the measurement of the thermionic constants reported in this paper. The two white marks set off the portion of the crystal upon which the measurements were taken.

toward the cooler outer portions. Thus crystals are obtained which occupy the whole cross section of the wire and retain the preferred orientation of their parents.

Presumably a crystal seed with its (110) crystal axis coinciding with the axis of the wire now exists in the wire at the surface of the mercury in tube A. Tube C is then sealed off at the constriction H leaving tube A and tube B connected only by tube D. The pressure in tube Ais reduced slightly thus insuring an "overlap" of the seed. The thin-walled tube F is then broken by the magnetic hammer G, thus connecting the capillary leak L and the mercury manometer M, which is across the capillary, to tube B. A Hyvac pump is connected to J through an adjustable leak, thereby maintaining the pressure difference across the capillary leak at any desired value under one atmosphere.

During the rest of the process, the wire is held at 2600°K. Since the wire is immersed in hydrogen, a very steep temperature gradient exists at the surface of the mercury. As the hydrogen is slowly removed from tube *B* through the capillary leak *L*, the mercury slowly falls in *A*, thereby moving the steep temperature gradient down the length of the wire and extending the crystal seed with it. A temperature of 2600°K and lowering speeds of 1 inch per hour down to $\frac{1}{6}$ inch



FIG. 4. Cross section and top view of tube used to measure the thermionic constants for the different crystal directions. This shows the single crystal wire A mounted in the rotor R so that it can be rotated in front of the slit S cut in the side of the cylindrical ancde B.

per hour were found to give fairly satisfactory results.

After the mercury lowering process is completed, the wire must be heated for several hours in hydrogen at the advanced temperature of about 2950°K to absorb into the body crystal numerous small surface crystals.

After the completion of the heat treatment the wire is transferred to an electron projection tube. These tubes were developed by Johnson and Shockley¹ and later further by Nelson² and Martin.³ Fig. 2 taken from Nelson's thesis shows a typical one-dimensional projection tube. The applied electric field between the filament and the fluorescent screen is radial, so that if a sufficiently high field is used, the thermal electrons emitted by the filament travel in straight lines radially to the screen. Thus, the illumination at any part of the screen is a qualitative measure of the emission of the portion of the filament having the same cylindrical coordinates of azimuth and distance along the wire axis provided, of course, that the filament is round.

A regular pattern on the fluorescent screen possessing the symmetry properties of a cubic crystal with one of its face diagonals along the axis of the screen (two reflection planes at right angles) indicates the presence of a single crystal in the corresponding position on the wire.

Figure 3 is a photograph of a projection tube in which was mounted the wire upon which the thermionic measurements set forth in the following section of this paper were made. The large single crystal is about 9 cm long. The two horizontal lines show the region of the wire from which the thermionic data were taken. Photomicrographs of the surface of the wire will be shown in the next section.

Precautions are necessary to obtain a smooth surface on the recrystallized wire. The hydrogen must be free from oxygen, water vapor, and hydrocarbon vapors because these active etching agents give a very rough surface to the wire. It is for these reasons that the crystal-growing apparatus was designed in the form set forth above, since in this form each step can be carried out with the requisite cleanliness and purity of materials.

Apparatus for Measuring the Thermionic Constants of Single Crystal Wire

The tube used to make the quantitative thermionic measurements was designed and constructed by Dr. R. B. Nelson but was rebuilt to incorporate certain refinements. The metallic parts of the tube are all of tantalum except for leads and springs. The envelope is of Pyrex.

Figure 4 is a schematic diagram of the metallic parts of the tube. A sufficiently high voltage is applied between the single crystal filament Aand anode B to cause the thermal electrons from the filament to proceed radially in straight lines to the anode B. Those electrons whose trajectories are in line with the slit system SS' pass through to the collector D and are measured. The radial voltage gradient in the neighborhood of the wire A must be large compared to the local gradients set up by the differences of work function of the various crystal directions. Also, the voltage must be high enough to render insignificant the initial thermal velocities of the electrons. The lower voltage limit of the tube turned out to be about 1000 volts. The upper limit set by field emission difficulties is about 3500 volts. Between these limits the tube showed no polarization or leakage difficulties. In this voltage range a negative potential of 800 volts relative to the anode B on the electrode C was found to eliminate slow secondary electrons from the slits SS' and to keep slow secondaries from leaving the collector D. A positive potential of 180 volts on the guard rings G keeps stray electrons from reaching the lead to the collector. The rotor frame R supports the wire A and is pivoted at the points PP' with tungsten pivots and glass bearings. Rotor R can be rotated about PP' from outside the tube by causing an electromagnet to attract the laminated soft iron rod I which is sealed in a Pyrex envelope, thus bringing the different crystal directions of the single crystal in A into alignment with the slit system SS'.







FIG. 6. Schottky plot for the (111) direction. Δ Data at 1890°K; o data at 1450°K.

The mirror M permits the measurement of the angles through which the crystal has been rotated. The tantalum spirals KK' serve to conduct the heating current through the wire and yet permit the free rotation of the rotor R. The glass insulator F which supports the collector system D is of special design.⁵ The resolving power of the slit system and the optical system used to measure the angles through which the crystal is rotated is about three degrees.

The whole metallic system is suspended from a single tungsten-to-glass press; all the remaining leads, of which there are six, are flexible thus permitting the glass envelope to change its shape freely, as it does to a certain extent during the baking process, without throwing any of the parts out of alignment. The tube was gettered with barium-aluminum getter and sealed from the vacuum system before the measurements were taken. The technique used in the preparation of the structural parts for vacuum and the schedule of evacuation have been described by Nottingham.6

The direct current used to heat the filament Awas supplied from storage batteries and accurately measured by use of a Leeds and Northrup type K potentiometer and a standard tenth-ohm resistor. The diameter of the wire, which must be accurately known, was measured by an interferometer and checked by weighing a measured length. From the value of the density of tungsten given by Jones and Langmuir,7 these two methods agree to within two-tenths percent.

⁵ W. B. Nottingham, Phys. Rev. 55, 203 (1939)

⁶ W. B. Nottingham, J. App. Phys. **8**, 762 (1937). ⁷ H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310, 354, 408, (1927).



FIG. 7. A, photomicrograph of single crystal wire looking down the (001) direction; B, ten degrees off the (110) direction.

The Forsythe-Watson⁸ temperature scale was used to determine the temperature of the middle section of the wire A. Over the range used, no end corrections were needed. The anode-tofilament voltage was supplied from a filtered kenotron rectifier and measured by use of the type K potentiometer and a precision voltage divider. The electrometer method used to measure the collector current over a range of 10^{-5} to 10^{-14} ampere is described by Nottingham.⁵

EXPERIMENTAL RESULTS

By rotating the single crystal wire to different positions in front of the slit system SS', the yield of thermal electrons from the different directions can be measured. The dependence of emission upon crystal direction is shown in Fig. 5A at 1880°K and in Fig. 5B at 1480°K. The emission before the wire was heated above 2500°K, after mounting in the final tube, is given by the combination of dotted and solid lines. For angles where the dotted lines do not show, the emission remained constant through further heat treatment. The solid lines show the values after heat treatment up to 2650°K. Little is known about the behavior of single-crystal surfaces undergoing heat treatment in a vacuum. Because of the possibility of an irreversible change in the surface structure at higher temperatures, a complete set of data was taken after the 2650°K flashing but before the wire was raised to higher temperatures. It is upon this set of data that the thermionic constants which are tabulated in the following are based. There was no need for re-

 8 W. E. Forsythe and E. M. Watson, J. Opt. Soc. Am. 24, 114 (1934).

peating the measurements since the emission at any point did not change more than 5 percent even after an aggregate of 6 minutes at 2900°K and 2 minutes at 2960°K. The 30-second, 2900°K flashes were alternated with ten to twelve-hour heatings at 1800° to 2000°K.⁹ The data collected here indicate, to the extent of the heat treatment given the wire during the measurement period, that no surface changes which affect the thermionic properties have taken place.

The polar emission diagrams show perfect symmetry of a cubic crystal with one of the face diagonals along the axis of the wire. The angles at which the various crystal directions cut the surface of the wire have been calculated and drawn into the polar diagram. To within the resolving power of the slit system and the optical system for measuring the angles (about 3°) these crystal directions agree with the maxima and minima found. This shows the presence of a nearly perfect crystal in a round wire. A back reflection Laue x-ray photograph down the (111) crystal axis of the wire was taken and checked the crystal orientation. This assignment of crystal directions is in perfect agreement with the results of Martin's3 spherical system and Nelson's² cylindrical system, both sets of results having been corroborated by x-ray determination of the directions. Although the peaks of the two maxima on either side of the (001) direction occur very near the (116) directions, it is doubtful if they can be characteristic of any one given crystal direction because the (115), (117), etc.,

TABLE I. Thermionic constants for the various crystal directions of tungsten. The estimated error in the determination of the φ_0 is about 0.5 percent. This means that the error in A^* is about ten percent.

Miller Indices	φ0	A*	S
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4.37 4.35 4.36	36 41 30	12.5 11.5 13.0
$\begin{array}{cccc}1&1&2\\1&1&\overline{2}\end{array}$	$\begin{array}{c} 4.66\\ 4.66\end{array}$	125 125	$\begin{array}{c} 11.1\\11.2\end{array}$
$\begin{array}{cccc}1&1&6\\1&1&\overline{6}\end{array}$	4.35 4.36	56 51	$\begin{array}{c} 11.7\\ 10.7\end{array}$
$\begin{array}{ccc} 0 & 0 & 1 \\ \overline{1} & \overline{1} & 0 \end{array}$	4.53 4.65	117 15	10.5 9.6

⁹ E. A. Coomes, Phys. Rev. 55, 519 (1939).



FIG. 8. Composite Richardson plot for the different crystal directions on the same scale. The broken line represents the emission from the (111) direction.

crystal directions come so close to them. Nevertheless, they will be labelled as (116).¹⁰

To enable the reduction of the high field emission values to "zero field" values, the dependence of the emission on the anode filament voltage for each maximum and for each minimum occurring on the polar plot was investigated for two different temperatures. Fig. 6 is a representative plot showing the voltage dependence of the emission in the (111) direction at 1890°K and 1450°K. The two sets of data are superimposed to show the agreement of slope. The data follow the wellknown law derived from the Schottky mirrorimage theory:

$$\log_{10} i_v = \log_{10} i_o + SV^{\frac{1}{2}}/T$$

where i_v is the high field emission, i_o the "zero field" emission, and V the voltage. The constant S depends on the geometry of the emitter and collector system. For the system used here, assuming that the filament is perfectly round and smooth, the theoretical value of S is 10.5. Actual experimental values differ somewhat from this value presumably on account of surface irregularities of the wire. Surface projections will make for a larger S, whereas surface depressions of the order of magnitude of, or greater than, the resolving power of the collimating slits will make for a smaller S. The values of S as determined graphically from the Schottky plots for the various crystal directions are tabulated along with the other thermionic constants in Table I. These values of S were used to calculate the "zero field" emission i_o .

Figure 7A is a photomicrograph of the crystal wire looking down the (001) direction. This region of the wire is smooth and gives a value of S very nearly the theoretical value. Figure 7B is a photomicrograph taken ten degrees off the (110) direction and indicates a flat region normal to the (110) direction. This flatness explains the low S for this region. The furrowed surface on either side of the (110) direction extends nearly to the (111) direction. From an inspection of many specimens, it seems that this surface configuration is general for wire heat treated in the fashion set forth here.^{2, 11} Until more is known about the surface structure of tungsten filaments, it is better to think of the thermionic data presented



FIG. 9. Richardson plot for the three duplicate (111) directions. \bigcirc data for (111) direction. \square data for (111) direction. \triangle data for (111) direction.

¹¹ R. P. Johnson, Phys. Rev. 54, 459 (1938).

¹⁰ The work of Nelson, reference 2, and Martin, reference 3, did not point conclusively to the minimum in the (001) direction. However, Professor W. B. Nottingham has recently informed me that his projection tube data from aged crystals show a definite minimum in the (001) direction.

here as associated with different crystal directions rather than with the ideal crystal faces normal to these directions because one cannot as yet be sure that the actual surfaces normal to these directions are "pure," i.e., that an actual surface normal to a given crystal direction is made up solely of the ideal crystal face normal to this direction.

The temperature dependence of the emission from each maximum and each minimum was investigated. Using the values of S in Table I, the "zero field" emission can be calculated. These "zero field" values were fitted to the empirical formula

$$i_o = aA^*T^2 \exp\left[-e\varphi_0/kT\right],$$

where A^* and φ_0 are constants and a the area of the wire from which the emission comes. The value of a is calculated from the wire diameter and the dimensions of the slits. Fig. 8 is a composite plot of $\ln_{10} i_o/T^2$ versus $10^4/T$ for the various crystal directions showing the variation in slope and ordinates. Fig. 9 is a composite plot of the data from the three duplicated (111) directions. The two directions show good agreement, but the third, the $(11\overline{1})$ direction, exhibits higher ordinates but has the same slope as the other two. To within experimental error, the data for each direction lie on a straight line, φ_0 being determined from its slope. Knowing φ_0 , $\log_{10} A^*$ is computed by selecting any one point exactly on the straight line. As seen from Table I, the variation in emission is accounted for by changes in both A^* and φ_0 . For completeness it should be pointed out that Mendenhall and De Voe¹² under great experimental difficulties obtained the value of 4.35 electron volts for the photoelectric work function of a (310) crystal direction and 4.50 for a (112) direction.

Since there is a variation of 0.3 volt in the value of φ_0 over the various crystal directions, there will be relatively large tangential voltage gradients just outside the wire. For the case of the five-mil wire used here, the most rapid 0.3volt change takes place in about twenty degrees, assuming each different crystal face is pure, giving tangential gradients of the order of 150 volts per centimeter. However, the data upon which the φ_{10} are based were taken with radial gradients of 60,000 volts per centimeter, so the effect of the tangential fields is negligible.

The Schottky mirror image theory of the voltage dependence of work function holds for pure polycrystalline tungsten surfaces from a surface gradient of about 2500 volts per cm¹³ up to the order of a million volts per cm where field emission begins to set in. It is not unreasonable that the surface fields between the various crystal faces exposed cause the deviation of experiment from theory for gradients under 2500 volts per cm.¹⁴ Certainly, from the very nature of the theory, the agreement for lower gradients should get better, if the surface is homogeneous in nature, i.e., a single crystal face. Making the reasonable assumption that the Schottky mirror image theory is correct, for a surface of all one crystal face, down to zero field, the i_o really represent zero field emission. By this method of measuring i_v at high field and using the Schottky theory to extrapolate to zero field emission i_o , the effect of the neighboring crystal faces on the behavior of electrons emitted from a given face has been eliminated.

DISCUSSION

For a detailed interpretation of the empirical constants A^* and φ_0 the reader is referred to papers by Herzfeld,¹⁵ Wigner,¹⁶ and Becker and Brattain.¹⁷ The values of φ_0 reported here closely represent the work required to remove an electron from the top of the Fermi band at zero degrees Kelvin to a distance outside of a homogeneous crystal face, this distance being large compared to the lattice constant but small compared to the dimensions of the crystal face. The differences between the φ_0 for the different crystal directions may be interpreted as being caused by differences in the nature of the double layers formed on the various crystal faces. The double layers are set up by the lack of symmetry of the electron distributions around the surface ions, and are such that they generate a constant potential inside the metal. However, the potential

¹² C. E. Mendenhall and C. F. De Voe, Phys. Rev. 51, 346 (1937).

¹³ W. B. Nottingham, Phys. Rev. 49, 78 (1936).
¹⁴ J. A. Becker, Rev. Mod. Phys. 7, 95 (1935).
¹⁵ K. F. Herzfeld, Phys. Rev. 35, 248 (1930).
¹⁶ E. Wigner, Phys. Rev. 49, 696 (1936).
¹⁷ J. A. Becker and W. H. Brattain, Phys. Rev. 45, 694 (1936). (1934).

outside the metal is not constant but varies in such a way that the potential differences between the outer neighborhoods of different crystal faces are equal to the differences in the moments of their respective double layers.

As was mentioned before, the Schottky mirrorimage theory of the voltage dependence of the work function does not hold for polycrystalline tungsten surfaces for surface gradients under about 2500 volts per centimeter.¹³ Probably the most complete discussions of this deviation have been given by Becker¹⁴ and Nottingham.¹³ Becker found, if he assumed for a polycrystalline surface a checker board surface in which alternate checkers possessed different work functions, that the emission from such a surface would deviate from the Schottky theory in the same general way as actual polycrystalline surfaces have been found to deviate. In fact, if he chose the size of his checkers to correspond roughly to the grain size of polycrystalline tungsten wires (about 10^{-4} cm) and the difference in work function of adjacent checkers to be about 0.5 volt, he obtained good agreement with experiment for thoriated tungsten surfaces. Of course, the theory holds just the same for pure tungsten surfaces in which case it appears, from the data presented in Table I of this paper, that the differences in work function between the adjacent checkers should be of the order of several tenths of a volt. For a more detailed discussion the reader is referred to Becker's and Nottingham's papers; but it is perhaps not out of place to give a brief qualitative explanation of this deviation for pure polycrystalline tungsten on the basis of the data set forth in this paper.

Let x_0 be the distance from a plane homogeneous tungsten surface at which the image forces on the electron just equal the force of the externally applied electric field. Thus $x_0 = \frac{1}{2}(e/E)^{\frac{1}{2}}$. For E = 1,000,000 volts/cm, $x_0 = 19(10)^{-8}$ cm. For E = 60,000 volts/cm (the surface gradient at which the Richardson data for this paper were taken) $x_0 = 76(10)^{-8}$ cm, and at E = 2500volts/cm, $x_0 = 380(10)^{-8}$ cm. The different crystal faces appearing in this polycrystalline surface will be roughly the same size as the grains. For the polycrystalline samples upon which thermionic measurements have been made, the grain size is known to be about 10^{-4} cm. Table I shows

that the maximum difference in φ_0 between facets is at least 0.3 volt. On account of the difference in contact potential between neighboring facets, the potential for an electron just outside a facet of low work function will be lower than the potential outside a facet of high work function. Roughly speaking then, if x_0 is very small compared to the facet size (10^{-4} cm) , that is for high field strengths, the emission from a given facet will be relatively uninfluenced by the neighboring facets of different work function. However, when x_0 approaches the same magnitude as the facet size, then the emission from a given facet will be influenced by the difference in contact potential between the given facet and the neighboring facets. Most of the emission comes from the facets of low work function. On account of the presence of the neighboring facets of higher work function the field strength on the facets of lower work function is actually lowered so that the field strength on these facets is lower than the experimenter thinks. As x_0 becomes very large $(E \rightarrow 0)$, the work required to remove an electron from any crystal facet to a large distance becomes the same and the Schottky theory again holds. Therefore, the larger the facet size and the smaller the difference in work function the smaller become the surface fields at which the Schottky theory fails. Assuming the validity of an argument of this type, the deviation from the Schottky theory gives some idea of the nature of the surface of the emitter. For example, if the maximum difference in work function between neighboring facets is held constant, the smaller the size of the facets the higher will be the surface gradients for which the deviation from the Schottky theory sets in.

If the surface normal to a given crystal direction is not "pure," i.e., if it is made up of several different crystal faces, the φ_0 determined by the temperature dependence of its emission will be that of the crystal face of lowest φ_0 if the data give a straight Richardson line. Then the empirical A^* associated with this surface will be that associated with the crystal face of lowest φ_0 multiplied by the fraction of the surface area which is made up of the crystal face of lowest φ_0 . Table I includes several low values of A^* , the lowest being that for the (110) direction. Fig. 7B shows the roughness of this surface and also the



FIG. 10. Schottky plot for $(\overline{110})$ and (111) crystal directions.

roughness extending to the (111) directions. On account of this roughness these surfaces are presumably not pure. Fig. 10 is a Schottky plot for the (110) direction compared with that for the (112) direction which has a high A^* value. Microscopic examination (Fig. 7A) shows the surface normal the (112) direction to be smooth. The Schottky plot for the (110) direction deviates from the Schottky theory for a value of the surface gradient E of about 4.5×10^4 volts/cm $(x_0 = 90 \times 10^{-8} \text{ cm})$ whereas the Schottky plot for the (112) direction [as well as all other directions with the exception of the (110) direction] agrees with the theory down to much lower voltages.¹⁸ This deviation for the (110) direction shows that there is a small scale "checkerboard effect" on the surface normal to the (110) direction. This evidence together with the roughness of the surface indicates that the surface normal to the (110) direction is not "pure" which may account for the low A^* value associated with this direction. On this basis one would expect on the surface normal to the (110) direction the existence in considerable proportion of crystal faces whose work function is higher than 4.65 volts. Thus the values of A^* do not possess any unique physical significance but are strongly influenced by the lack of purity of the crystal surfaces as well as by inaccurate knowledge of the surface area,¹⁴ temperature variation of the work function^{13, 15, 16} and reflection effects.¹³

As seen from Table I, a considerable part of the surface of the single crystal wire has values of φ_0 as low as 4.35 electron volts. The average φ_0 over the whole crystal wire as given by the temperature dependence of the emission from the whole wire would be only slightly larger than this value of 4.35. The accepted value of this average φ_0 for tungsten wire not treated in the special manner outlined here is about 4.50 ev. This seems to indicate that the special heat treatment starting from polished wire exposes crystal faces which do not occur in appreciable degree in the ordinary samples of wire. However, the φ_0 given in Table I for the (001) crystal direction nearly coincides with the average value for ordinary wire.¹⁹ Furthermore, the empirical A* for ordinary polycrystalline unpolished tungsten wire is around 60. The Schottky data¹³ for this ordinary wire as well as the electron projection tube data¹ indicates the patchy nature of these surfaces showing that the value of 60 is really not characteristic of any of the pure crystal facets occurring in these samples.

Further work is under way to check the generality of the results reported here and to extend the measurements to thoriated and caesiated tungsten crystal surfaces.

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¹⁸ The surface gradients which exist even if the whole single crystal wire were made up of the pure crystal faces as well as the initial thermal velocities of the electrons spoil the "projection" properties of the tube for voltages under about 1000 volts.

¹⁹ R. P. Johnson, Phys. Rev. **54**, 459 (1938) reports that under certain conditions tungsten filament surfaces tend to expose mainly faces normal to the (001) crystal directions.



FIG. 3. Photograph of the projection tube in which was mounted the single crystal wire used for the measurement of the thermionic constants reported in this paper. The two white marks set off the portion of the crystal upon which the measurements were taken.



Fig. 7. A, photomicrograph of single crystal wire looking down the (001) direction; B, ten degrees off the (110) direction.