PHYSICAL REVIEW VOLUME 80, NUMBER 5 DECEMBER 1, 1950

Periodic Deviations in the Schottky Effect for Tantalum*

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(Received July 17, 1950)

Periodic deviations from the Schottky law in the thermionic emission from patchy surfaces of tantalum and thorium on tantalum have been measured for fields up to 3×10^5 volts cm^{-1}, and at temperatures of 1200 and 1500°K. The work function of the clean tantalum as determined by Richardson plots was 4.03 ±0.04 ev, and was changed by approximately 1/2 volt by thorium deposition. A method was found for separating the periodic deviations from the patch effects.

For clean tantalum the phase and amplitude of the deviations are in approximate agreement with the theory when the tunnel effect is neglected. The temperature variation was found to be in accordance with theory.

The thorium on tantalum caused the amplitudes of the deviations to decrease and the phase to shift toward lower fields. The decrease of amplitude seems to rule out the existence of a potential peak at a composite emitter surface of this type.

I. INTRODUCTION

PERIODIC deviations in the Schottky effect[1] have been reported for thermionic emission from tungsten[2–5] and from tantalum.[3] Mott-Smith[6] suggested that these deviations might be a quantum-mechanical effect. Upon this suggestion Guth and Mullin[7,8] derived expressions which describe the observed phenomenon as a function of the electric field, the temperature, and certain electronic properties of the emitter. It was also implied[7,8] that a patchy emitting surface might influence the observed deviations.

The present investigation was undertaken to study the effects of patches, temperature, and change of work function, and thereby to determine the applicability of the phenomenon to research upon the surface physics of solids. Thermionic emission from patchy surfaces of tantalum was measured at 1500 and 1200°K with collecting fields up to 3×10^5 volts cm^{-1}. The work function was altered by evaporating thin films of thorium from a thoriated tungsten filament upon the tantalum, and corresponding changes were observed in the periodic deviations.

II. PREVIOUS RESULTS

The Schottky law[1] for a uniform metal surface can be written as

$$I=I_0 \exp[e(eE)^{\frac{1}{2}}/kT], \tag{1}$$

where I is the emission current for the collecting field E, I_0 the zero field current, and T the absolute temperature of the emitter. From this equation it follows that the common logarithm of I plotted against the square root of E should be the straight line

$$\log I-\log I_0-C_0\xi/T=0, \tag{2}$$

where the constant C_0 is 1.914 deg. K (cm $\text{volts}^{-1})^{\frac{1}{2}}$, and $E^{\frac{1}{2}}$ is designated by the symbol ξ.

Experiments on tungsten[2–5] and tantalum[3] have indicated that the right side of Eq. (2) is not zero, but instead is an oscillating function of the field. Typical periodic deviations obtained experimentally by Turnbull and Phipps[4] are shown by the open circles in Fig. 1, where the amplitude F_2 is plotted against ξ. The amplitude and period increase with the applied field. A more complete examination of published data indicates that the amplitudes may increase with decrease in temperature without affecting the phase,[2–4] and that the deviations for tantalum appear to be the same as those for tungsten.[3]

The derivation of Eq. (1) is based on the assumption that all electrons within the metal moving toward the surface barrier have a transmission coefficient which is independent of the field. Since a humped potential barrier is formed outside the metal surface, quantum

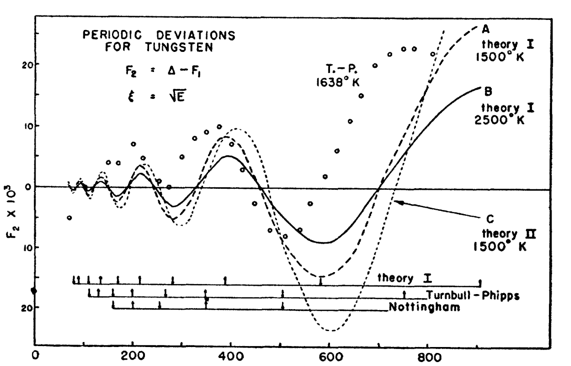

FIG. 1. Periodic deviations in the Schottky effect for tungsten. The theoretical curves are calculated for $W_a=10.3$ electron volts. Theory I neglects the tunnel effect which is included in Theory II. The arrows indicate positions of maxima and minima.

* This research was sponsored by the U. S. Navy Bureau of Ships.

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1 W. Schottky, Physik. Zeits. 15, 872 (1914).
2 R. L. E. Seifert and T. E. Phipps, Phys. Rev. 53, 493 (1938).
3 R. L. E. Seifert and T. E. Phipps, Phys. Rev. 56, 652 (1939).
4 D. Turnbull and T. E. Phipps, Phys. Rev. 56, 663 (1939).
5 W. B. Nottingham, Phys. Rev. 57, 935 (1940).
6 H. M. Mott-Smith, Phys. Rev. 56, 668 (1939).
7 E. Guth and C. J. Mullin, Phys. Rev. 59, 575 (1941).
8 E. Guth and C. J. Mullin, Phys. Rev. 61, 339 (1942).

TABLE I. Values of the constants for the Guth-Mullin theory (see Eq. (5)). Units for the field and temperature are volts cm^{-1} and deg. K respectively. W_a was taken as 9.27 electron volts for tantalum and 10.3 electron volts for tunsten. It was assumed $W_a=W_i+\varphi e$, where W_i is the chemical potential and φe the work function.

C's	General	Tantalum	Tungsten
$C_1\times 10^3$	-1.58	-1.58	-1.58
$C_2\times 10^3$	$-9.29W_a^{1/2}$	-28.2	-29.8
C_3	358	358	358
C_4	$-\frac{7.38}{W_a^{1/2}}+\frac{W_a^{1/2}}{14.8}-0.5$	-2.7	-2.5
C_5	$-\frac{7.38}{W_a^{1/2}}+\frac{W_a^{1/2}}{14.8}+0.3$	-1.9	-1.7

mechanics predicts the reflection[9] of some of the electrons with kinetic energies sufficient to escape in classical mechanics. Interference among the reflected electron waves leads to maxima and minima in the transmission coefficient as the height and thickness of the barrier vary with change of field. The quantum-mechanical probability that some electrons may tunnel through the barrier also contributes to the transmission coefficient. When allowance is made for the variation of transmission coefficient with field the Schottky law becomes

$$I=I_0[\bar{D}(E)/\bar{D}(0)]\exp[e(eE)^{1/2}/kT], \qquad (3)$$

where $\bar{D}(E)$ is the mean transmission coefficient for field E, obtained by averaging over the energy distribution of the emitted electrons and $\bar{D}(0)$ is the mean transmission coefficient for zero field. Then Eq. (2) becomes

$$\log I-\log I_0-C_0\xi/T=\log\bar{D}(E)-\log\bar{D}(0)=\Delta, \qquad (4)$$

where Δ represents deviations from the Schottky law. Guth and Mullin[7,8] computed Δ in Eq. (4) for the Maxwellian distribution of electrons transmitted through a barrier composed of an image potential combined with the potential due to the applied field. Their results may be written

$$\Delta=F_1+F_2 \qquad (5a)$$

where according to this theory, the deviation Δ is composed of two functions of E: the periodic function F_2, and the monotonic function F_1 about which F_2 oscillates. If the tunnel effect is neglected,[7] then F_1 is given approximately by

$$F_1=C_1\xi^{3/4}/T \qquad (5b)$$

where C_1 is a universal constant of the order 10^{-3} deg. K (cm $volts^{-1})^{3/4}$. When the tunnel effect is added, according to the theory[8] F_1 reduces to a negligibly small quantity.

[9] S. Dushman, *The Elements of Quantum Mechanics* (John Wiley and Sons, Inc., New York, 1938), Chapter 3.

The complete expression for the periodic term F_2 is

$$F_2=\frac{C_2\xi^{3/4}}{T}\left[\frac{1}{f_1}\cos\left(\frac{C_3}{\xi^{1/2}}+C_4\right)+\frac{1}{f_2}\cos\left(\frac{C_3}{\xi^{1/2}}+C_5\right)\right], \qquad (5c)$$

where the second cosine term results from taking into account the tunnel effect and reduces to zero if this effect is neglected. The slowly varying functions f_1 and f_2 in formula (5c) are

$$f_1=[(15.1+0.158\xi^{3/4}/T)^2+88.9]^{1/2}, \qquad (5d)$$

$$f_2=[(30.2-0.158\xi^{3/4}/T)^2+88.9]^{1/2}, \qquad (5e)$$

if the field is in volts cm^{-1} and the temperature in deg. K. To a good approximation C_1, C_2, C_3, C_4, and C_5 are constants for a given emitter, whose computation as well as that of the functions f_1 and f_2 involve only natural physical constants. Computed values are listed in Table I.

The function $F_2=\Delta-F_1$ should represent the experimentally observed periodic deviations from the Schottky line. Computed curves for F_2 in the case of tungsten are displayed with the experimental data in Fig. 1. Curves A and B have been computed for tungsten at 1500 and 2500°K respectively, neglecting the tunnel effect. Curve C includes the tunnel effect at 1500°K.

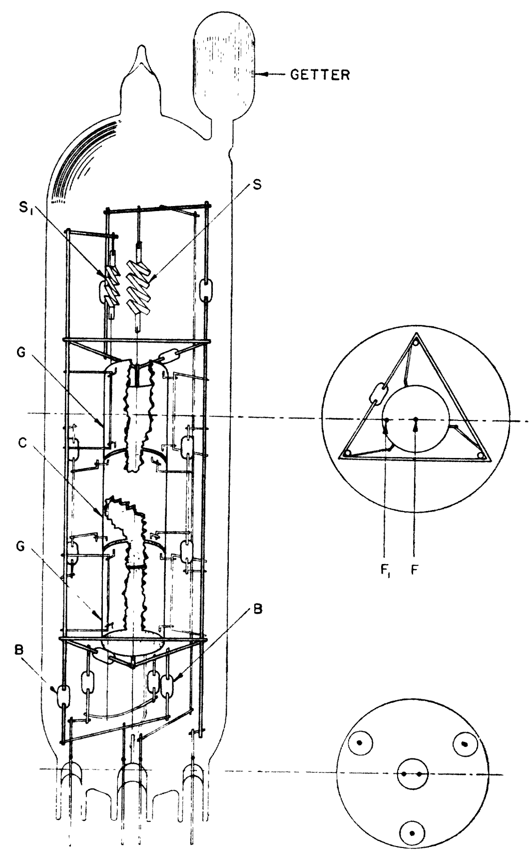

FIG. 2. Experimental tube for studying deviations in the Schottky effect for thermionic emission from filaments.

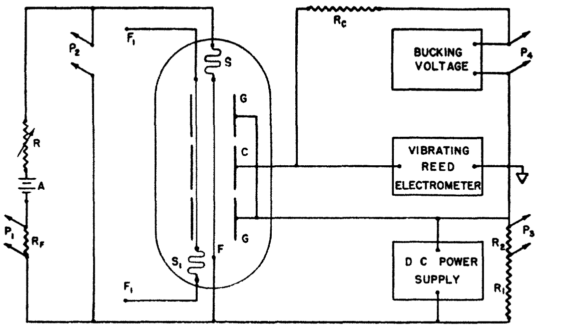

FIG. 3. Circuit diagram. The vibrating reed electrometer is used as the null indicator.

General features agree, but at higher fields a large phase difference occurs between computed and experimental curves. This is particularly apparent when positions of the extrema, indicated by the arrows in Fig. 1, are compared; the data of Turnbull and Phipps[4] are consistent with those of Nottingham,[5] but both are at variance with the theory when fields reach the order of 10^5 volts cm^{-1}, even when the tunnel effect is neglected.

III. EXPERIMENTAL METHOD

Tube Construction

The present study of Schottky deviations was made on fine-grained unpolished filaments of tantalum.[10] Figure 2 shows the construction of the experimental tube. The 0.001-inch tantalum filament F is held taut along the axis of the coaxial collector-guard-ring-system CGG by the molybdenum spring S. The diameter of F was determined within 0.2 percent by weighing measured lengths and using the value of 16.60 g cm^{-3} for the density.[11] The collector and guard rings were tantalum cylinders 2 cm in diameter and 3 cm long. The source of thorium was the thoriated tungsten filament[12] F_1 held taut by spring S_1 and located near the collector to minimize distortion of the field at the cathode F. Mechanical precision was attained by mounting the tube elements on the beaded framework, upon which centering and aligning were done independently of the glass envelope. The 7052 glass beads BB were able to withstand a cathode to anode potential difference of 15 kv and maintain a leakage conductance of less than 10^{-15} mhos. Essentially standard procedure[13] was followed in the preparation of parts for vacuum and in pumping the tube and outgassing the parts during evacuation. The tube was sealed off at a pressure

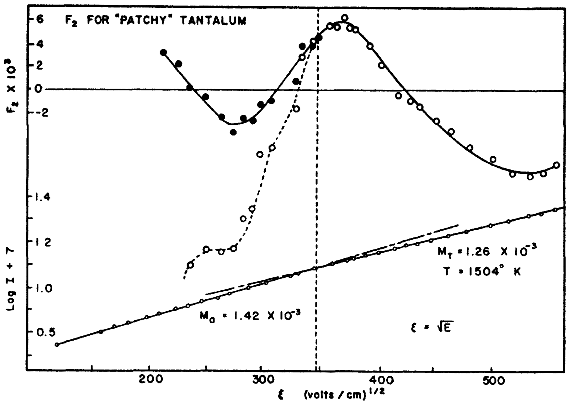

FIG. 4. Periodic deviations about a patch break. The slope of the normal Schottky region is M_T; the slope of the anomalous region is M_a.

of 2×10^{-8} mm of Hg, measured by a conventional type ionization gauge, after barium getter[14] was flashed in the end bulb illustrated in the drawing. The tantalum filament was cleaned and stabilized by 10-minute periods of flashing at 2350°K. After the source filament F_1 was flashed initially at 2900°K for one hour for outgassing and for reducing the thoria, it was maintained at 2500°K for the evaporation of thorium. At this temperature it required about 20 hours to deposit a fraction of a monatomic layer of thorium sufficient to reduce the work function of clean tantalum by approximately one-half volt. During evaporation periods the receiver filament F was held at 1500°K to encourage migration over its surface.[15] Even at this temperature it required about one-half hour after F_1 was turned off to complete the migration process and obtain an equilibrium state of the emitter system.

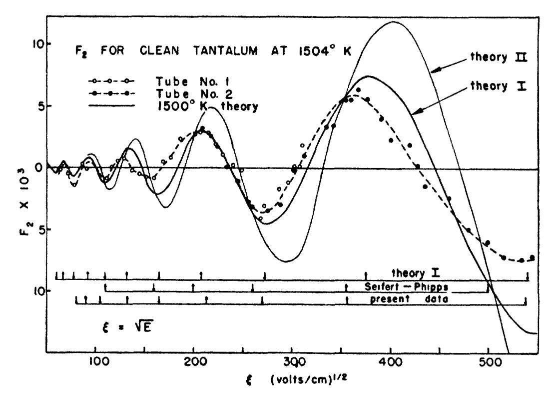

FIG. 5. Periodic deviations for clean tantalum. The theoretical curves are calculated for $W_a=9.3$ electron volts. Theory I neglects the tunnel effect which is included in theory II. The arrows indicate positions of maxima and minima.

[10] Experiments now in progress on highly polished 0.005-inch tantalum wires have revealed no differences in the deviations for polished or unpolished filaments.
[11] L. Malter and D. B. Langmuir, Phys. Rev. 55, 743 (1939).
[12] The thoriated tungsten wire was furnished by the Cleveland Wire Works of the General Electric Company through the courtesy of Mr. W. M. Rossington.
[13] W. B. Nottingham, J. App. Phys. 8, 762 (1937).
[14] The getter was KIC type 61018F, furnished by the Kemet Laboratories of Cleveland, Ohio, through the courtesy of Mr. Milo Wells.
[15] C. J. Gallagher, Phys. Rev. 65, 46 (1944).

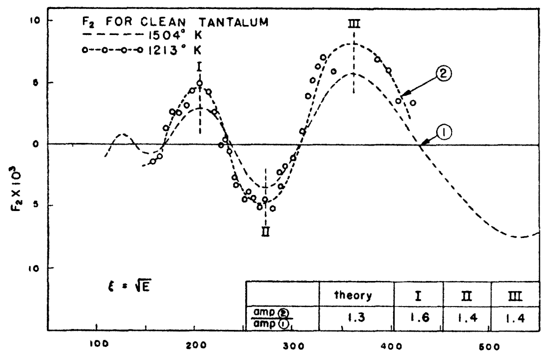

FIG. 6. The temperature dependence of the periodic deviations for clean tantalum. Curve (1) for 1504 deg. K is transferred from Fig. 5. Both curves (1) and (2) are drawn as the best fit to experimental data. The theoretical ratio of the amplitudes is computed from the inverse temperature relation (see Eq. (5)).

Electrical Measurements

The measuring circuit is represented by the block diagram in Fig. 3. The temperature of the filament F was obtained from the Malter-Langmuir[11] tables of the $V'A'^{\frac{1}{3}}$ function; the voltage across the filament was measured by the potentiometer P_2, and the heating current was determined from the voltage across the standard 1-ohm resistor R_F measured by the potentiometer P_1. While the absolute value of the temperature is not accurate[11] to better than 10°K, constancy of temperature was checked during the taking of emission data by monitoring the filament heating current and voltage. The filament current was supplied by a bank of five lead storage batteries connected in series and operated on the part of their discharge characteristic over which the voltage was constant. The batteries were inspected daily and the specific gravity kept between 1.200 and 1.250, in order to keep the current stable over any one run. The variation in temperature during a run was no greater than 0.2 percent.

The magnitude of the field at the cathode F opposite the midpoint of the collector was found from the collector voltage, which was obtained from potentiometer reading P_3 across a section of the calibrated voltage divider R_2R_1. The current was determined by balancing out the ohmic drop across the resistor R_c, and reading the balancing voltage was potentiometer P_4. The null indicator was an Applied Physics Corporation Model 30 Vibrating Reed Electrometer,[16] which had remarkable stability. In the present application currents of 10^{-11} amp. were measured reproducibly to a precision of 10^{-14} amp. The high resistance R_c could be adjusted to 0.1008, 1.185, 12.10, 120.0, or 1580 megohms by switching. The high resistance components were S. S. White resistors mounted on Teflon standoff insulators of shunt resistance greater than 10^{15} ohms; these components were checked periodically against a Leeds and Northrup 1000.0-ohm standard resistor. The maximum error in the emission current determinations is estimated at 0.1 percent.

IV. EXPERIMENTAL RESULTS

Effect of Patch Fields

Schottky plots of the emission data usually exhibited patch breaks,[17] as shown in Fig. 4. The slope for the higher fields checked the value C_0/T computed from the temperature, while the anomalous slope had a larger value, as expected from patch theory. In each field region the slope M and the intercept $\log I_0$ were determined graphically and the periodic deviations computed as the quantity $F_2 = \log I - \log I_0 - M\xi$; the slope and the intercept in a given region of constant slope must be used to compute the experimental values of F_2 in that region. This is illustrated in Fig. 4, where the open circles are the deviations computed using M_T alone. In this case there is a drifting of points below the break, which does not occur if the slope and intercept appropriate to the region are employed. When the anomalous slope M_a is used for the lower fields, the computed deviations represented by the closed circles in Fig. 4 are obtained.

Clean Tantalum

The value of 4.03±0.04 ev obtained for the thermionic work function of tantalum by means of Richardson plots was taken as evidence for an uncontaminated surface.[18] Experimental curves of F_2 for clean tantalum are shown in Fig. 5 and Fig. 6. Figure 5 shows a comparison of experimental and theoretical curves for 1500°K. The open and closed circles in Fig. 5 represent data from two different experimental tubes, corrected for the patch effect by the method described in the preceding section. The arrows indicate positions of the extrema according to Seifert and Phipps,[3] the theory,[7] and the present results.

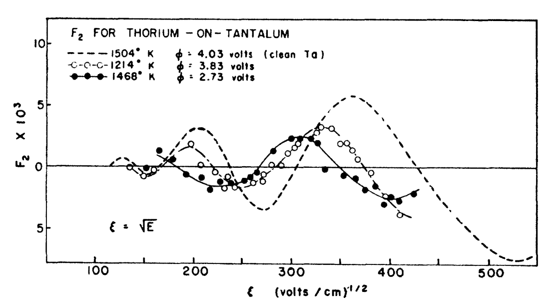

FIG. 7. Periodic deviations in the Schottky effect for thin films of thorium on tantalum. The values of work function were determined experimentally by Richardson plots. The amplitudes decrease and the extrema shift to lower values of applied field with decrease in work function.

[16] Palevsky, Swank, and Grenchik, Rev. Sci. Inst. 18, 298 (1947).

[17] C. Herring and M. H. Nichols, Rev. Mod. Phys. 21, 185 (1949), Chapter 2.

[18] Dushman, Rowe, Ewald, and Kidner, Phys. Rev. 25, 338 (1925).

In Fig. 6 the experimental curve for 1504°K is drawn as the reference curve. The open circles in Fig. 6 represent the experimental results at 1213°K. The phase is unaffected by the decrease in temperature, but the amplitudes of the periodic deviations have increased. The ratios of the amplitudes at three extrema are listed in the table in the figure.

Thorium on Tantalum

In Fig. 7 the experimental F_2 deviations for thorium on tantalum are compared with those for clean tantalum. As the work function of the filament was decreased from 4.03 to 3.83 to 2.73 ev, not only did the amplitudes decrease in each instance, but the extrema of the deviations also shifted to lower values of applied field.

V. DISCUSSION

The mean positions for the maxima and minima in F_2 for clean tantalum are listed in Table II for the present experiment. Over the range of fields studied these data for the phase of the deviations are in fair agreement with theory if the tunnel effect is neglected. The experimental amplitudes are always less than theoretical (Fig. 5), this discrepancy increasing at the higher fields.

The two important aspects of lowering the emitter temperature are encountered when the deviations observed at 1213°K for a clean tantalum filament are compared with the 1504°K data taken on the same filament. First, the amplitudes as shown in Fig. 6 increase inversely with temperature, in substantial accordance with the theory. This may be brought out by comparing the ratios of the amplitudes at the three principal extrema, which has been done in the table in the figure. Secondly, it may be observed that experiment reveals no change in phase as the temperature is changed, which is also implied by the theory whether or not the tunnel effect is included.

The principal effects experienced when the work function of the tantalum surface was lowered by thin films of thorium were two: (a) the amplitudes of the periodic deviations decreased, and (b) the positions of the extrema shifted to lower values of field. These results are displayed in Fig. 7. Herring[19] has pointed out that the existence of a peak in the potential barrier near the surface of a composite emitter, which has sometimes been surmised, should become noticeable through an *increase* in the amplitudes of the periodic deviations. The *decrease* in amplitudes exhibited by the present data does not substantiate the existence of such a barrier modification for thorium on tantalum, within a range of work functions from 4.03 to 2.73 ev.

The shift of extrema to lower fields and the decrease in amplitudes when thorium is deposited on clean tantalum may be accounted for in part by a decrease in W_a with decrease in work function. This can be seen qualitatively from an examination of Eq. (5), where W_a occurs in such a manner in both the amplitude factor C_2 and in the phase factors C_4 and C_5 that a decrease in W_a implies a simultaneous decrease in amplitudes and a shift in extrema to lower values of ξ.

[19] C. Herring and M. H. Nichols, Rev. Mod. Phys. **21**, 185 (1949), Chapter 4.

TABLE II. Positions of the maxima and minima in the periodic deviations for clean tantalum in terms of $E^{\frac{1}{2}}$ (volt cm^{-1})$^{\frac{1}{2}}$. The maxima are given in italics.

Observed by Seifert and Phipps[a]	Observed by Munick, LaBerge, and Coomes	Computed from the Guth-Mullin theory[b] neglecting tunnel effect
	80	78
	90	*92*
	104	110
110	*132*	*132*
160	164	164
200	*206*	*208*
260	267	273
355	*364*	*374*

[a] See reference 3.
[b] See reference 7.

VI. CONCLUSIONS

The results of this experiment tend to establish the following points. (a) The temperature variations for periodic deviations are as theory predicts, namely an inverse variation of the amplitude with no shift in phase. (b) The deposition of a thin film of thorium on a clean tantalum surface does not produce a potential peak, since the addition of the thorium decreases rather than increases the amplitudes of the deviations. The data seem to indicate that the theory in its present state accounts for the fundamental physical factors involved in periodic deviations from the Schottky effect; probably a revision in the basic theoretical model to include such details as the atomic structure of the surface and of the interior of the metal would lead to more exact quantitative agreement.

The authors gratefully acknowledge the help of Dr. C. Herring and Mr. George E. Moore of the Bell Telephone Laboratories. Dr. Herring offered many helpful suggestions during the course of the work, and together with Mr. Moore read and criticized the manuscript. Thanks are expressed to Mr. H. W. Weinhart of the Bell Telephone Laboratories for his assistance with the filament structures. We also wish to thank Mr. Ernest Parsons and Mr. Fay Gifford of our own group for their technical assistance in carrying out the experiment and in preparing the manuscript.

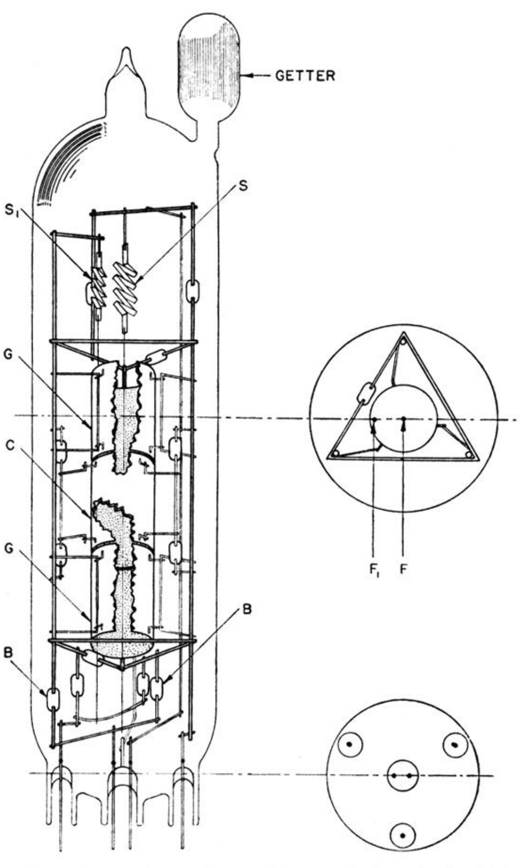

FIG. 2. Experimental tube for studying deviations in the Schottky effect for thermionic emission from filaments.