(A18) may be written in the form

$$\mathcal{P} = ne^2\tau(E^0)^2 \int_0^\infty dP_H \sum_{m=0}^\infty \sum_{\rho,\sigma} \omega_{m+1,\sigma;m,\rho}$$

$$\times (\rho_{m,\rho}{}^{(0)} - \rho_{m+1,\sigma}{}^{(0)})(y_{m,\rho;m+1,\sigma})^2$$

$$\times \left(\frac{1}{1+\tau^2(\omega+\omega_{m+1,\sigma;m,\rho})^2} + \frac{1}{1+\tau^2(\omega-\omega_{m+1,\sigma;m,\rho})^2} \right). \tag{A19}$$

The density matrix $\rho_{m,\rho}{}^{(0)}$ must now be written as

$$\rho_{m,\rho}{}^{(0)} = \exp\left[-\frac{\beta eHh}{mc}E_{m,\rho}{}^{(0)}\right] \bigg/$$

$$\left\{ 2\int_0^\infty dP_H \sum_{n=0}^\infty \sum_\sigma \exp\left[-\frac{\beta eHh}{mc}E_{n,\sigma}{}^{(0)}\right] \right\}. \tag{A20}$$

The subscripts ρ and σ refer to the eigenvalues attached to each quantum state n. The absorption line shape for a single transition, say from m,ρ to $m+1,\sigma$ will be denoted by $\mathcal{P}_{m,\rho;\sigma}$ and, neglecting the coefficient, may be written as

$$\mathcal{P}_{m,\rho;\sigma}$$

$$= \int_0^\infty dP_H\, \omega_{m+1,\sigma;m\rho}(y_{m,\rho;m+1,\sigma})^2$$

$$\times \left[\exp\left(-\frac{\beta eHh}{mc}E_{m,\rho}{}^{(0)}\right) - \exp\left(-\frac{\beta eHh}{mc}E_{m+1,\sigma}{}^{(0)}\right) \right]$$

$$\times \left(\frac{1}{1+\tau^2(\omega+\omega_{m+1,\sigma;m,\rho})^2} + \frac{1}{1+\tau^2(\omega-\omega_{m+1,\sigma;m\rho})^2} \right)$$

$$\times \left[1 \bigg/ \int_0^\infty dP_H \sum_{n=0}^\infty \sum_\nu \exp\left(-\frac{\beta eHh}{mc}E_{n,\nu}{}^{(0)}\right) \right]. \tag{A21}$$

The line-shape curve for $P_H = 0$ is just the integrand taken at $P_H = 0$.

Reflection of Slow Electrons from Tungsten Single Crystals, Clean and with Adsorbed Monolayers

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The reflection of electrons with kinetic energy up to a few electron volts from tungsten single-crystal surfaces is measured both on the clean surface and with adsorbed monolayers of nitrogen and oxygen. For the clean surface, diffraction from the lattice is responsible for a considerable part of the reflection in the thermionic range of energy. The magnitude of the reflection is such as to have a barely measurable effect on experimental tests of the thermionic emission equations. This technique permits continuous recording of the change in work function as gas is adsorbed, yielding information about the kinetics of chemisorption and the surface dipoles due to the adsorbed gas atoms.

INTRODUCTION

THE well-known theoretical expression for the current density of thermionic electrons is[1,2]

$$J = A(1-\bar{R})T^2 \exp(-\varphi/kT), \tag{1}$$

where A is 120 amp/cm² deg², $\bar{R}$ is the reflection coefficient averaged over the energy distribution, and φ is the work function. If the assumptions leading to this equation are valid, the energy distribution is Maxwellian except for the factor R, which may depend on the energy. MacColl[1,3] calculated R using a one-dimensional model with a sinusoidal internal potential connecting

smoothly with an image potential at the barrier. He found about 5% reflection at zero kinetic energy of approach, falling rapidly at higher energy, with regions of 100% reflection very close to the energies where diffraction maxima are to be expected from the periodicity of the internal potential. The width of the region of 100% reflection in his examples is approximately equal to the amplitude of the sinusoidal internal variation in potential energy. It is, in fact, generally true in the weak-binding approximation that the width of the forbidden region is approximately equal to the matrix element of the periodic potential.[4]

For a more realistic model, one would expect to observe diffraction due to the three-dimensional space lattice. The effective mass, which enters into the calcu-

[1] C. Herring and M. H. Nichols, Revs. Modern Phys. **21**, 185 (1949).
[2] W. B. Nottingham, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, p. 1.
[3] L. A. MacColl, Bell System Tech. J. **30**, 588 (1951).
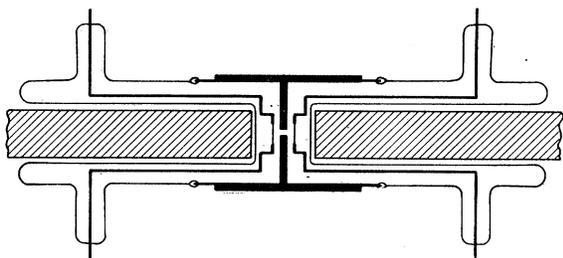[4] P. A. Wolff (private communication).

FIG. 1. Simplified diagram of the experimental tube. Shaded
areas represent the pole pieces of the magnet.

lation of the energy of the diffraction, depends on the
band structure near the vacuum level. A theoretical
value for the barrier height would depend both upon
a band-structure calculation and a calculation of the
surface dipole layer. The reflections due to diffraction
would be reduced to less than 100% by taking electron-
electron and other collisions into account. Since no cal-
culation taking these effects into account is available,
we will content ourselves with a qualitative experimental
correspondence with this model.

As for experimental investigations of the reflection
coefficient, Nottingham,[2,5] from the analysis of his data
on polycrystalline tungsten wire, proposed

$$R = \exp(-V/0.19), \quad (2)$$

where V is the kinetic energy in electron volts, due to
the velocity component, outside of the metal perpen-
dicular to the surface. Herring and Nichols[1] pointed
out that this form of reflection has no theoretical basis
and is, in fact, in conflict with the interpretation of
experimental results on periodic deviations from the
Schottky effect. They suggested that his results were
the consequence of patchiness, such as had been investi-
gated by Becker and Brattain,[6] probably due to the
polycrystalline nature of the surface. It was apparent
that meaningful results could be obtained only if the
experiment were performed on a single-crystal plane.
Hutson[7] measured the energy distribution of thermionic
electrons from a single-crystal wire and found that his
data were fitted quite well on each of the planes in-
vestigated by the reflection given in Eq. (2). Smith[8]
pointed out that Hutson's results could be explained
without such a reflection if the resolution were 10 times
poorer than estimated, but no source of such poor
resolution has been found. However, Shelton[9] has since
performed an experiment on the (211) plane of tantalum
in plane parallel geometry and found an extremely
sharp "knee" on a plot of log I vs V, showing only an
8% reflection nearly independent of energy in the range
of interest. Thus, it appears likely that Nottingham's

reflection was due to patch effects originally, and its
apparent confirmation by Hutson was due to instru-
mental limitations.

A modification of Shelton's tube has been constructed
as part of a program investigating the adsorption of
gases on metal. Evidence is given that the above-
described "more realistic" theoretical model is, in
essence, correct, and that Nottingham's reflection does
not fit the experimental results for tungsten, the sub-
stance for which it was proposed and apparently con-
firmed. As a part of this study the effect of the adsorp-
tion of nitrogen and oxygen on the reflection from, and
the work function of, the (310) face of tungsten is also
reported.

APPARATUS AND EXPERIMENTAL PROCEDURE

Shelton's tube consisted of two single-crystal ribbons,
the emitter at thermionic temperature and the collector
at room temperature, separated by the accelerator, a
diaphragm with a small hole, which was kept at a
positive potential with respect to the emitter. A mag-
netic field collimated the electron beam, thus attaining
a good approximation to infinite plane parallel geometry.

The most important modification in the present tube
was to make the accelerator the divider between two
separately pumped compartments so that the hot
emitter could be kept in a lower pressure of gas than the
collector and therefore be maintained as a stable
reference while adsorbable gas was admitted to the col-
lector. The tube was made re-entrant for strength and
this feature was used to bring the pole pieces of the
magnet as close as possible to the working parts, as
shown in Fig. 1. The magnetic field was roughly 8000
gauss. The hole in the diaphragm was a circle 0.025 mm
in diameter cut with a high-energy electron beam
through a 0.25-mm sheet of stainless steel. Other details
of the geometry were also different from those in Shel-
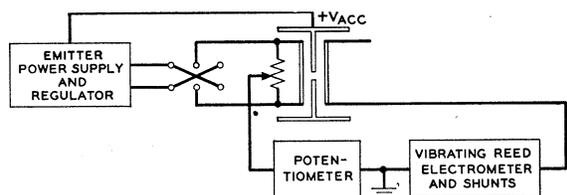
CIRCUIT 1. RETARDING POTENTIAL AND REFLECTION EXPERIMENTS
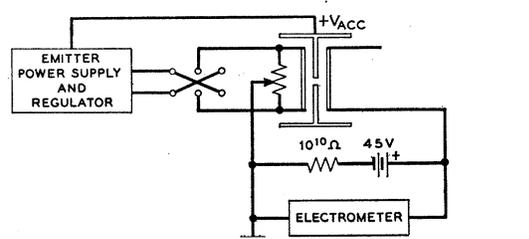
CIRCUIT 2. OBSERVING CONTACT POTENTIAL DIFFERENCE
AS A FUNCTION OF TIME

FIG. 2. Circuits in which the tube of Fig. 1 was employed.

[5] W. B. Nottingham, Phys. Rev. **49**, 78 (1936).
[6] J. A. Becker, Revs. Modern Phys. **7**, 95 (1935).
[7] A. R. Hutson, Phys. Rev. **98**, 889 (1955).
[8] G. F. Smith, Phys. Rev. **100**, 1115 (1955).
[9] H. Shelton, Phys. Rev. **107**, 1553 (1957) and dissertation,
M.I.T., Cambridge, Massachusetts, 1956).

ton's experiment, the ribbons being thinner (0.025 mm) and closer to the accelerator (2 mm). The ribbons were grown into single crystals by passage under tension through a steep temperature gradient. The surface orientation was determined by back-reflection Laue x-ray analysis.

The vacuum systems for the two sides attained ultimate vacuums below 10^{-10} mm Hg according to the Bayard-Alpert-type vacuum gauges. No increase in pressure was observed on the emitter side when the pressure on the collector side was raised from 10^{-10} to 10^{-6} mm Hg of nitrogen or oxygen, which is consistent with the leak rate through the small hole computed from its dimensions.

Block diagrams of the two circuits in which this tube was used are shown in Fig. 2. In the first circuit the point on the resistor shunting the emitter which was at the same potential as that portion of the emitter supplying the current through the hole to the collector was found by setting the potentiometer to a voltage on the retarding portion of the curve and adjusting the tap on the shunt until there was no change of collector current when the heating current was reversed. In the second circuit the 45-v battery and the 10^{10}-ohm resistor act as a constant current source. When the temperature of the emitter is so high that the saturated emission current to the collector is greater than the constant current supplied, the voltage from emitter to collector adjusts itself in the retarding range to oppose the battery. As gas is adsorbed on the collector

FIG. 4. The lower trace gives the pressure while the upper trace shows the work function with an arbitrary zero. After a series of cleaning flashes at the beginning, the collector is allowed to accumulate adsorbed gas in the continuous-flow system for a time long enough for the pressure to return to its steady-state value (see text).

and the work function changes, the voltage across the tube changes so as to keep the external field in the accelerator-collector space constant. This voltage, which therefore follows the changes in contact potential difference, is measured by the electrometer which draws a current negligible compared to that through the tube.[10] The change in contact potential can thus be continuously recorded on a strip-chart recorder.

A circuit regulated the emitter temperature to keep the current to the accelerator constant. Two regulator circuits were used, one using transistors and the other vacuum tubes in a circuit developed from that used by Shelton. Both worked satisfactorily, but the tube circuit could be adjusted to regulate smaller currents than the transistor circuit.

An example of the kind of information contained in the data of a run with the first circuit of Fig. 2 is shown in Fig. 3. We plot the logarithm of the collector current against the applied voltage. The slope in the retarding range gives us the temperature of the emitter. The voltage at the point of intersection between the retarding and saturated portions gives us the work-function difference between the hot emitter and the cold collector, subject to a small thermoelectric correction. The current at this point of intersection, together with the temperature of the emitter and the area of the hole, allows a calculation of the work function φ of the emitter, using Eq. (1), providing some assumption is made about $\bar{R}$, to which, however, for behavior in reasonable agreement with experiment, it is insensitive. Variations of current in the saturated region yield information about electron reflection.

The tube used was ill adapted to measuring the absolute work function of the emitter because the small hole through the relatively thick accelerator caught some of the spiraling electrons on the sides, and the
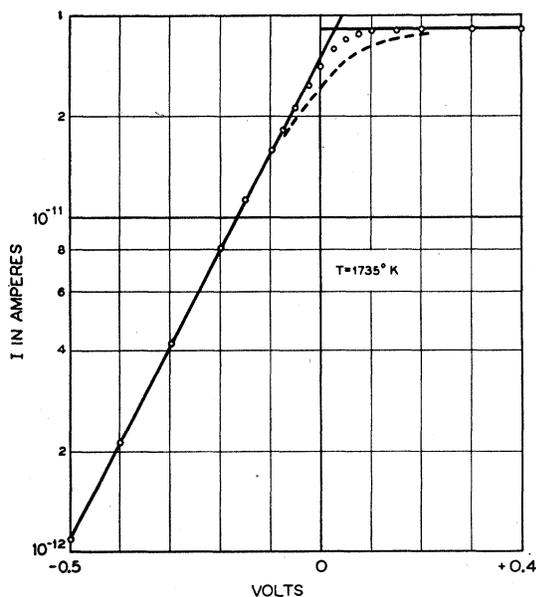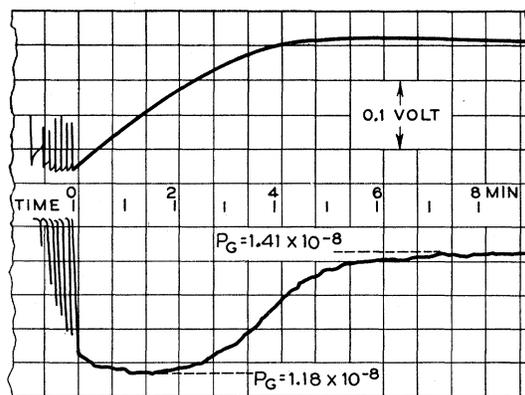

FIG. 3. Experimental points showing "knee" at the intersection of retarding and saturated parts of the logarithm of the collector current plotted against applied voltage. Intersecting solid lines are theoretical for $R=0$, which was very nearly obtained by Shelton (see footnote 9). Dashed curve is the result of applying Nottingham's reflection [Eq. (2)] to both emitter and collector.

[10] C. R. Crowell and R. A. Armstrong, Phys. Rev. 114, 1500 (1959).

heater current of the emitter produced an appreciable magnetic field at the accelerator, so that the beam did not go straight down the axis of the hole. Consequently, the effective area of the hole was only about one-sixth of the apparent area. The hole was made small so as to minimize the effect of the potential drop along the heater ribbon in order to obtain as sharp a "knee" as possible.

EXPERIMENTAL RESULTS

A typical experimental retarding potential plot is shown in Fig. 3. While it is apparent that Nottingham's correction is excessive, we were not able to obtain the extremely sharp knee reported by Shelton, even with the tiny hole, probably for reasons depending on tube- and ribbon-geometry. If we assume that the discrepancy is not instrumental, we might seek the explanation in microscopic patchiness. A conceivable source of such patchiness would be a surface sawtooth in cross-sectional shape so that simpler planes of different work function would be exposed instead of a smooth plane in the apparent orientation (310). The electron microscope revealed no such structure larger than the resolution of the replicating technique which is of the order of 100 A.

Let us now turn to the experiments on gas adsorption using the second circuit of Fig. 2. Nitrogen has been shown in previous experiments to dissociate into atoms when adsorbed on tungsten.[11,12] The contribution of each adsorbed atom to the change in work function is proportional to the component perpendicular to the surface of the dipole moment between adatom and
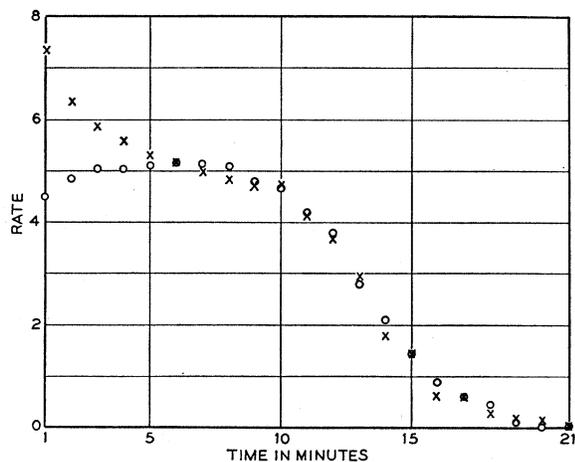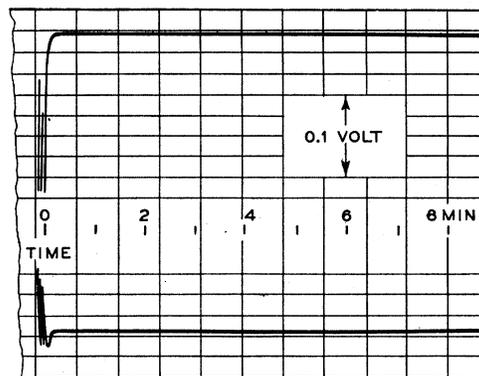

FIG. 6. As in Fig. 4, but for a pressure about 20 times greater.

substrate. If this quantity is constant, the rate of change of work function is proportional to the rate of adsorption. In a continuous flow system the reduction in pressure below its steady-state value is also proportional to the rate of adsorption. The pressure gauge was separated from the experimental tube by a considerable pumping impedance, so that the changes in measured pressure were relatively small, but they could be made apparent by depressing the zero and increasing the amplification. A simultaneous record of the increment in work function and in pressure is shown in Fig. 4. After a number of short cleaning flashes, the pressure is reduced by the pumping action of the ribbon, but for an interval of about a minute the pressure continues to fall as the glass walls give up some of the gas they adsorbed during the cleaning flashes. Finally, as the monolayer is nearly completed, the sticking probability decreases and the pressure rises towards its asymptotic steady-state value. Over this same time interval the work function begins at its clean-surface value, rises almost linearly for a while, then becomes nearly constant. Figure 5, using the results of a similar run at lower pressure, compares the rate of adsorption as measured from $d\varphi/dt$ and from $(P_\infty - P)$. The curves are arbitrarily normalized to agree at the point at 6 min. The disturbance due to adsorption on the glass causes disagreement in the expected direction for a time, but after this the agreement is good, showing that the dipole moment per molecule remains constant from $\frac{1}{4}$ monolayer to a full monolayer.

After this adsorption the work function remains quite constant even at much higher pressures, so long as the gas is pure. An example of a higher pressure run is shown in Fig. 6. A slow drift is sometimes observed when there is reason to suspect that impurities may be present in the nitrogen gas, for example, when gas from a bottle at atmospheric pressure has been stored in an intermediate reservoir at about 1 mm Hg for several days before being admitted to the system. Under the cleanest circumstances, however, an exposure of 6×10^{-5} mm Hg-min failed to produce any further measurable change in work function (i.e., less than 0.005 v) after the initial exposure caused a change of 0.2 v in about 5×10^{-8} mm

FIG. 5. $d\varphi/dt(x)$ and $(P_\infty - P)(0)$ vs time after flashing for a (310) face of tungsten in nitrogen starting with a clean surface flashed to 2300°K. Both quantities are, in principle, proportional to the rate of adsorption if the dipole moment per molecule is constant. The curves are arbitrarily normalized to agree at the point at 6 min.

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[11] T. W. Hickmott and G. Ehrlich, J. Phys. Chem. Solids **5**, 47 (1958).

[12] P. Kisliuk, J. Chem. Phys. **30**, 174 (1959).

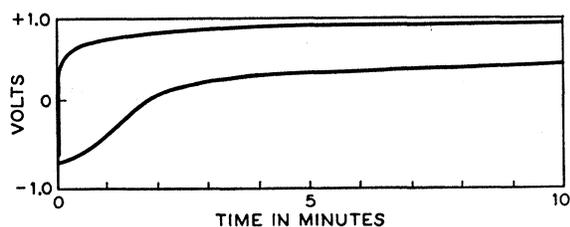FIG. 7. φ (with an arbitrary zero) as a function of time after flashing for a (310) face of tungsten in oxygen. The lower curve is for a relatively low pressure corresopnding roughly to that of Fig. 4 and the upper one for a higher pressure corresponding roughly to that of Fig. 6. Note that the scale of work function is less sensitive than that of Figs. 4 and 6 by a factor of eight.

Hg-min. While this result may not hold for other crystal surface orientations, in the author's opinion reports in the literature of chemisorption of nitrogen on tungsten beyond the first monolayer at a coverage for which the sticking probability is very small (say, less than 10^{-3}) are open to the suspicion of being due to impurities.[13,14]

To convert the observed change in work function into a dipole moment per W-N bond involves the density of atoms in the completed layer. If there were a simple 1-1 correspondence between tungsten atoms in the (310) plane and adsorbed nitrogen atoms, this number would be 6.3×10^{14} atoms/cm^2. Experimentally on a similar ribbon a coverage of 4.2×10^{14} atoms/cm^2 has been observed,[15] the discrepancy possibly being due in part to the orientation being one or two degrees off. We thus obtain a dipole moment between 0.085 and 0.12 Debye unit, corresponding to a separation for a singly charged ion of only 0.02 A from the equipotential plane. This small moment is undoubtedly due to a combination of small spacing and a largely covalent bond.[16]

For oxygen the change in work function on the (310) face is much greater than for nitrogen, $\Delta\varphi$ being 1.7 v and still slowly increasing at the greatest exposure tried, 10^{-5} mm Hg-min. The increment in work function as a function of time due to oxygen at two different pressures is shown in Fig. 7 on a scale eight times less sensitive than that of Fig. 5. The correlation of $d\varphi/dt$ with pressure is much poorer with O_2 than with N_2 because of greater adsorption on the glass walls, and possibly also because of the production of some CO from carbon in the ribbon.[11,18] The quantity of oxygen adsorbed was not measured in this experiment, but Eisinger[19] found

that almost twice as much oxygen as nitrogen was adsorbed on his (311) ribbon. If this were also true for the (310) plane, the dipole moment would be about 0.45 Debye unit.[20]

Let us now consider some of the background information necessary in the interpretation of the electron reflection data. This apparatus measures the total collected current, which is the current which arrives at the collector diminished by the reflected current and the secondary emission current, which return to the accelerator. (We neglect multiple reflections.) A number of workers[22–26] have shown that electrons returning from a surface bombarded by electrons can be divided into these two groups—those elastically reflected, which lose but a small fraction of their initial energy, and the secondaries which retain but a small fraction of their initial energy. This nomenclature is, to some extent, arbitrary because there is, of course, no way of distinguishing a true reflected primary from any other electron of the same energy, and there is a measurable number of electrons at intermediate energies, but the electrons do divide naturally into these two groups. Secondaries appear in measurable numbers only when the kinetic energy of approach is greater than the work function.[23–25] The number in each class
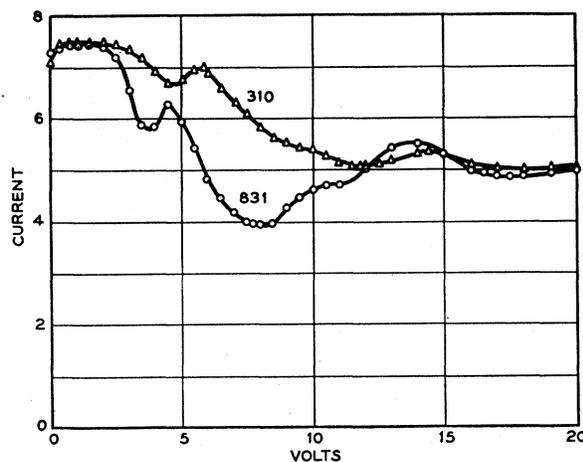

FIG. 8. Collector current vs applied collecting voltage in the acceleration region for two clean tungsten surfaces of the indicated orientations.

[13] J. Eisinger, J. Chem. Phys. 28, 165 (1958).
[14] P. L. Jones and B. A. Pethica, Proc. Roy. Soc. (London) 256A, 454 (1960).
[15] P. Kisliuk (unpublished).
[16] To compare our result ($\Delta\varphi = +0.20$ v) with other values in the literature, Eisinger (see reference 13) finds $\Delta\varphi = 0.35$ v for the rapidly adsorbed nitrogen on the (311) plane. For the coverage he reports, this corresponds to a dipole moment of 0.16 Debye unit. On polycrystalline tungsten, Mignolet (see reference 17) finds $\Delta\varphi = 0.50$ v for a complete layer, while Jones and Pethica (see reference 14) obtain $\Delta\varphi = 0.2$ v at completion of the fast stage of adsorption.
[17] J. C. P. Mignolet, Rec. trav. chim. 74, 685 (1955).
[18] R. E. Schlier, J. Appl. Phys. 29, 1162 (1958).
[19] J. Eisinger, J. Chem. Phys. 30, 412 (1959).

[20] The value of $\Delta\varphi$ we find for the adsorption of oxygen on the (310) surface is in good agreement with the values obtained on polycrystalline tungsten (see footnote 17) and of the order of that found for various planes by means of the field emission microscope (see footnote 21).
[21] J. A. Becker Advances in Catalysis (Academic Press, Inc., New York, 1955), Vol. 7, 136.
[22] I. M. Bronshtein and V. V. Roschin, Soviet Phys.—Tech. Phys. 3, 2023 and 2271 (1958) (transl.).
[23] A. R. Shulman and E. I. Makinin, Soviet Phys.—Tech. Phys. 1, 2157 (1956).
[24] N. D. Morgulis and D. A. Gorodetskii, Soviet Phys.—JETP 3, 535 (1956).
[25] G. A. Harrower, Phys. Rev. 104, 52 (1956).
[26] H. A. Fowler and H. E. Farnsworth, Phys. Rev. 111, 103 (1958).

Table I. Calculated reflections from the (310) face of tungsten.

E_i(volts)	Reflecting plane
9.4	(110)
16.7	(100)
27.6	(211)
37.6	(310)

is roughly equal at 10 v, and above this the secondaries are more numerous than the reflected electrons. There is some structure to the yield of each class as a function primary energy, but the maxima and minima are more pronounced for the reflected electrons.[22,25,27]

Turning now to our experimental data, the collector current is plotted against collector voltage for two clean surfaces of different orientation in Fig. 8. We note first that there is a considerable dependence on surface orientation. We attribute the dips in the curves to reflection and will attempt to correlate them with diffraction effects.

Now in applying a diffraction theory, one needs a value for the inner potential V_0 which, to some approximation is $\mu + \varphi$, where μ is the depth of the Fermi sea. Electrons passing through the lattice with different momenta will, in general "see" different average potentials, especially if exchange and correlation effects are taken into account, so that V_0 is not, in theory, a fixed constant of the material. For tungsten, Manning and Chodorow[28] calculated 6.4 v for μ, neglecting exchange and correlation. Although Callaway,[29] in a review article, considers their approximations so severe that he sets little store by their numerical results, experiment indicates that this value is quite reasonable.[30,31] Taking $\mu = 6.5 \pm 1$ v and $\varphi = 4.5$ v, we find 11 ± 1 v for V_0. Burns[27] finds his data fitted satisfactorily by $V_0 = 12$ v and Cutler and Gibbon[32] fit the experimental deviations from the Schottky effect on polycrystalline tungsten with $V_0 = 10.3$ v.

Let us consider a beam of electrons incident normally on a (310) face of tungsten with kinetic energy inside the metal E_i (implying kinetic energy $E_i - V_0$ outside). We enumerate the lowest energy reflections from planes which are at such an angle as to reflect the electrons back out of the surface. In lieu of any preferable theoretical value we assume the free electron mass. If the above estimate of V_0 is correct, electrons reflected from the (110) plane cannot arrive from outside, and the lowest energy reflection would be that at $16.7 - 11.0 = 5.7$ v, reflected from the (100) plane and leaving the crystal at an angle of 35 deg above the surface plane. A dip near 5.0 v which we will ascribe to this reflection

[27] J. Burns, Phys. Rev. 119, 102 (1960).
[28] M. F. Manning and M. I. Chodorow, Phys. Rev. 56, 787 (1939).
[29] J. Callaway, in Solid-State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 100.
[30] J. A. Bearden and T. M. Snyder, Phys. Rev. 59, 162 (1941).
[31] H. D. Hagstrum, Phys. Rev. 96, 336 (1954).
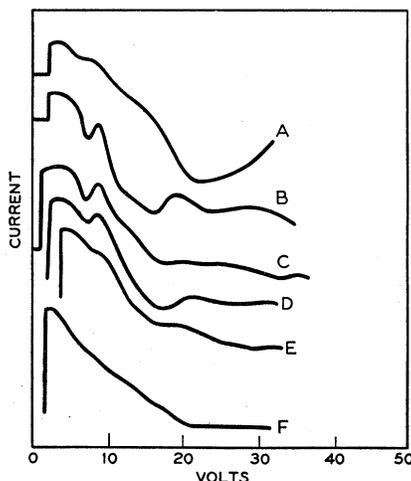[32] P. H. Cutler and J. J. Gibbon, Phys. Rev. 111, 394 (1958).

Fig. 9. Collector current vs applied collecting voltage traced from experimental recordings. The maximum current near 1 v is nearly the same for all curves, but they have been displaced vertically so that they can be displayed in a single figure. Horizontal "feet" on curves A-C represent the constant current collected during the time before the voltage drive was turned on. A is for an orientation midway between (411) and (210). B is for a surface less than 1 deg from the (310) orientation. C is for an orientation about 3 deg from the (310) orientation. Comparison between these three clean surfaces again illustrates the dependence on orientation. D is for the same surface as C after monolayers of oxygen had been adsorbed and flashed off repeatedly, a process known to roughen the surface somewhat. E is for the same surface as C and D after adsorption of a heavy layer of oxygen. Note that most of the distinguishing dips of curves C and D are still present at the same voltage, though diminished, but that the cut-off has moved about 2 v to the right. F is for the same surface as C and D with an adsorbed monolayer of nitrogen.

is apparent on the (310) curve of Fig. 8. The beginning of a dip visible near 0 v may be the wing of the (110) reflection, and the dip near 12 v could be the (211) reflection predicted at 16 v. For the (831) ribbon of Fig. 8, the only reflection predicted in this energy range is a (100) reflection at 6.4 v which might be identified with the observed dip at 8 v. This leaves the sharp dip at 4 v unexplained.

For the (211) face of tantalum, one would expect in the experimental energy range just one reflection normal to the surface at 10 v. Shelton[9] observes no such reflection, and the dips he does observe are smaller than those reported here by a factor of about five. From the data on reflection from gas-covered surfaces to be considered shortly, these results could be explained if there was a monolayer of impurity on the tantalum of Shelton's experiments in spite of his rigorous treatment.

In Fig. 9, tracings of the experimental curves of collector current are shown for various surfaces as described in the caption. In particular, compare curves C and D taken on a clean (310) ribbon with curve E taken on this same ribbon with an adsorbed layer of oxygen. The dips are somewhat obscured, but remain at practically the same voltage, while the work function barrier cuts off the curve about 2 v higher. Curve F is for this same surface with a complete layer of nitrogen. The change

in work function is too small to be apparent on this scale, but the diffraction features are obscured even more effectively than by oxygen.

The maximum current near 1 v on these curves corresponds to a reflection of about 8%, a value agreeing with that of Shelton,[9] and of the order found on other clean single crystal surfaces.[26] It is within the range which could be accounted for by reflection from the image barrier.[1,3] The best resolved dip due to diffraction has a width at half maximum of about 1.5 v and corresponds to an increase in reflection of 10% of the primary current. If such a reflection were situated so as to have maximum effect on the total emission the apparent value of A [Eq. (1)] would be reduced by about 20% from its theoretical value for $\bar{R}=0$. This is close to the value observed by Bulyginski,[33] though a part of the reflection he observes on a polycrystalline evaporated film must be due to patch effects. If such a diffraction were situated so as to introduce a maximum distortion of the energy distribution, the deviation from the Maxwellian distribution would be about 2% over an energy range for which the exponential factor causes a reduction of 300%. In other words, a measurement of the temperature by the slope of log T vs V in the retarding region might be in error by as much as 1% due to energy dependent reflection. On MacColl's model, assuming the free electron mass, this reflection corresponds to $V_0=11.5$ v, and V_1, the amplitude of the internal sinusoidal variation in potential, $=1.5$ v. The other reflections correspond to a larger value of V_1.

Now let us consider the change of the work function with temperature. The intersection of the retarding potential line with the saturated current line for clean (310) surfaces with the emitter at 2000°K occurred at 0.10±0.02 v, showing that the hot surface had a higher work function than the cold. This should be corrected for the change in chemical potential: $\Delta\mu=\int_{T_1}^{T_2}(d\mu/dT)dT$, where $d\mu/dT$, the thermoelectric power, is $\int_0^T(\sigma/T)dT$ and σ is the Thompson coefficient. No new measurements of $d\mu/dT$ or σ have been made at low temperatures in recent years, but Lander[34] has extended the measurements of σ to higher temperatures subsequent to Herring's estimate of $\Delta\mu$ some years ago.[1,35] A rough graphical integration shows that Herring's estimate is still valid and that about 30% of the apparent shift in $\Delta\varphi(\sim30$ mv) can be attributed to

this effect, so that assuming linearity from 300° to 2000°K, $d\varphi/dT=4\times10^{-5}$ v/deg, also of the order of magnitude estimated by Herring and Nichols.[1]

SUMMARY

To summarize the main results of these experiments:

(1) Nottingham's empirical reflection coefficient has once more been shown to be incorrect, this time on tungsten, the substance for which it was proposed and apparently confirmed by Hutson.

(2) Variations in reflection coefficient have been correlated to some extent with expected diffractions. Discrepancies are probably due to the crudeness of the theoretical model, and may disappear for a suitably refined calculation of the band structure. That the observed features are internal in origin is shown by the way they remain fixed in position relative to the Fermi level as the work function is changed by the adsorption of oxygen. That they are directionally dependent is shown by their differences on various crystal faces.

These reflections are generally broad enough and numerous enough to obscure a quantitative experimental test of the calculated value of the reflection coefficient due to the surface barrier alone. The order of magnitude of the observed reflections is such that the error introduced in the thermionic equations by assuming R to be zero are of the same order of magnitude as the present limitations to experimental precision.

(3) The changes in work function of a particular crystal plane due to the adsorption of gas can be followed continuously and correlated with the amount adsorbed. The presence of a monolayer of gas obscures the diffraction features without, as mentioned above, changing their position in energy.

(4) The temperature derivative of the work function has been measured for the (310) face of tungsten and found to be well within the range of theoretical estimates.

[33] D. G. Bulyginski, Soviet Phys.—Tech. Phys. 3, 683 (1958).
[34] J. J. Lander, Phys. Rev. 74, 479 (1948).
[35] C. Herring, Phys. Rev. 59, 889 (1941).