It is of interest to compute from the above data what are the values of the moments of inertia $I_x^{(e)}$, $I_y^{(e)}$ and $I_z^{(e)}$ effective in the states ν_2 and $2\nu_2$ for comparison with the values predicted by the relations (8). To do this we have confined ourselves to the use of the rotation-vibration energies up through $J=3$ since in these states the centrifugal distortion is small so that the energy relations (1) may be regarded as fairly rigorous. The values $\frac{1}{2}(1/I_x^{(e)}+1/I_y^{(e)})$, $-\frac{1}{2}(1/I_x^{(e)}+1/I_y^{(e)})+1/I_z^{(e)}$ and $\frac{1}{4}(1/I_x^{(e)}-1/I_y^{(e)})$ were averaged over these states, a little more weight being given to the values for which $J=2$ and $J=3$ since the constants will there be less affected by the inaccuracies of measurement. The coefficients of centrifugal distortion which were used were those calculated on a purely theoretical basis. The results of this calculation are to be found in Table V.

It will be seen that the agreement between the calculated and observed values of the moments of inertia effective for ν_2 and $2\nu_2$ as well as for Δ is consistently better than that arrived at by Darling and Dennison on the basis of the earlier data available to them on these bands. The improved values for the fundamental band and the new ones deduced from our analysis of the overtone band $2\nu_2$ represent a satisfactory bit of verification of the theory of the water vapor molecule.

I desire to express my gratitude to Dr. W. H. Shaffer of this laboratory who has verified several of the steps leading to the results herein contained. A grant-in-aid from the Rumford Fund is also acknowledged with gratefulness.

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Electron Emission of Metals in Electric Fields

I. Explanation of the Periodic Deviations from the Schottky Line

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The periodic deviations from the Schottky line observed by Phipps and his collaborators and by Nottingham in measuring the thermionic emission of electrons from tungsten and tantalum can be interpreted as being due to the partial reflections of the electron waves on the potential hill at the surface of the metal. These partial reflections give rise to interference and thus to a periodic term in the transmission coefficient for the escaping electrons. The transmission coefficient is obtained by using the functions of the parabolic cylinder to establish the connection between the asymptotic expansions of the wave functions to the left and right of the top of the potential hill. The calculated positions of the maxima and minima of the deviations agree very well with the observed positions. In agreement with experiment, it is found that the positions of the maxima and minima are sensibly independent of temperature; and the amplitude decreases as the temperature is increased. The calculated amplitude of the deviations increases with the field, as does the observed amplitude. A dependence upon the work function of the emitting metal is obtained; however, since the heights of the surface potential barriers of tungsten and tantalum are very nearly equal, no experimental data on this dependence are available.

I. Introduction

When electrons are emitted from a metal by the application of heat, or of an electric field, or of both simultaneously, one has the following expression for the emitted electron current

$$i=\int_0^\infty N(W)D(W,F)dW, \tag{1}$$

where $N(W)$ is the number of electrons with energy W normal to the emitting surface. $N(W)$ is given by the Fermi distribution in the energy, which holds for the electrons in the metal; and $D(W, F)$ is the transmission coefficient for the electrons incident on the potential barrier at the metal surface with energy W normal to the surface. The potential field which the emitted

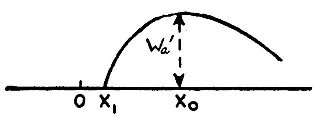

FIG. 1. The potential barrier traversed by the electrons. The metal surface is at $x=0$. For $x<x_1$, $V=0$; for $x>x_1$, $V=W_a-1/2x-x/2x_0^2$.

electrons must traverse may be, with good approximation, taken to be

$$V=\text{const.}=0 \qquad \text{inside the metal,} \tag{2a}$$

$$V=W_a-e^2/4x-eFx \qquad \text{outside the metal (but not right up to the surface),} \tag{2b}$$

where W_a is the difference in the potential of the electron inside the metal and at infinity when $F=0$; F is the electric field applied to the metal surface; x is the distance of the electron from the metal surface, which is placed at $x=0$; and e is the electronic charge. The term $e^2/4x$ is the "image potential" which results from the attractive force exerted on the escaping electron by the induced charge $+e$ in the metal.[1–3] The term eFx is the potential due to the external electric field used to attract the electrons over to the collector. Equation (2b) will not hold right up to $x=0$ (i.e., the metal surface), where it has an infinity. The true potential outside the metal very probably goes to zero and joins smoothly to the line $V=0$, at $x=0$. We may closely approximate the true potential by modifying (2) as follows:

$$V=\text{const.}=0 \qquad x\leqslant x_1, \tag{3a}$$

$$V=W_a-e^2/4x-eFx \qquad x>x_1, \tag{3b}$$

where $x_1\sim e^2/4W_a$ is the point at which the external potential goes to zero, i.e., where it crosses the x axis. The discontinuity which has been introduced in the potential at x_1 does not exist in nature, of course, but since in the neighborhood of x_1 the true potential changes appreciably in a distance comparable to the de Broglie wave-length of the electrons, it may be accurately represented with this discontinuous one. The introduction of a more complicated potential function which would go smoothly to zero at $x=0$ would not appreciably alter our results, but would greatly complicate our calculations. Also, for our present purposes we have neglected the periodic variation of the potential inside the metal; our inner potential is an average over the periodicities.

If, for convenience, the following system of atomic units is adopted: unit of length $=a=h^2/me^2=0.528\text{A}=$ radius of first Bohr orbit in hydrogen; unit of energy $=e^2/2a=13.54$ ev $=$ ionization potential of hydrogen, Eq. (3) becomes

$$V=0 \qquad x\leqslant x_1, \tag{4a}$$

$$V=W_a-1/2x-x/2x_0^2 \qquad x>x_1, \tag{4b}$$

where x_0, the position of the maximum of the potential, is determined from the equation $e^2/4x_0=eFx_0$. The potential of Eq. (4) is shown in Fig. 1.

So long as intense (greater than 10^6 volts cm^{-1}) electric fields are not applied to the metal, the electrons whose energies are less than that corresponding to the maximum height of the barrier (W_a' in Fig. 1) are not pulled from the metal. In this case the electron current obtained is due to electrons whose energies are greater than W_a'; this emission is called thermionic or thermionic field emission. Thus, for thermionic emission Eq. (1) becomes

$$i(F,T)=\int_{W_a'}^{\infty}N(W)D(W,F)dW, \tag{5}$$

where W_a', the maximum barrier height at the field F, is given by

$$W_a'=W_a-1/x_0.$$

The term $1/x_0$ represents the amount the barrier has been lowered by the field F. This gives us the well-known Richardson equation for thermionic emission:

$$i=A_0\bar{D}(F)T^2e^{-\chi'/kT}, \tag{6}$$

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[1] We presume here, of course, that so long as the electron is some distance away from the metal surface, the surface may be considered smooth, so that this simple image law holds. Similarly, we assume one work function for the surface. Actually, each electron energy has its own potential barrier (reference 2) and each crystal face at the metal surface has its own work function (reference 3), the largest contributions to the current coming from the facets or spots of lowest work function. Agreement of experiment with the Schottky theory, which assumes the image law, justifies the first assumption. In all work of this type with emission phenomena, it seems reasonable to assume a weighted average work function.

[2] J. Bardeen, Phys. Rev. **49**, 653 (1936); **58**, 727 (1940); or cf. F. Seitz, *Modern Theory of Solids*, (McGraw-Hill, New York, 1940), p. 163 and pp. 394 *ff*.

[3] M. H. Nichols, Phys. Rev. **57**, 297 (1940).

where $\chi' = \chi - 1/x_0$; χ is the thermionic work function for $F=0$; i.e., $\chi = W_a - W_i$, where W_i is the width of the Fermi band at $T=0$; A_0 is the emission constant; T is the absolute temperature; and $\bar{D}(F)$ is the transmission coefficient summed over all energies in the Maxwellian distribution, to which the Fermi distribution reduces for electrons with energies greater than W_a'. If i_0 is the current one obtains for a given temperature with zero external field, then one has

$$\log i_F - \log i_0 = \log \frac{\bar{D}(F)}{\bar{D}(0)} + \frac{e^{\frac{3}{2}}}{kT} F^{\frac{1}{2}}. \quad (7)$$

Assuming for the moment that the transmission coefficient does not change appreciably with the field, one has the result that plotting $\log i_F$ against $F^{\frac{1}{2}}$ should yield a straight line; this line is known as the Schottky line. Equation (7) may be expected to hold rather exactly for fields which are not too small or too large, i.e., in the range $3\times 10^3 < F < 10^6$ volts cm^{-1}. For fields below $F=3000$ volts cm^{-1}, Eq. (7) does not hold because of "patchy emission." For fields greater than $F=10^6$ volts cm^{-1}, Eq. (1) does not reduce to Eq. (5); in other words, with intense fields, electrons whose energies are less than W_a' are pulled from the metal and tunnel through the potential barrier; so again Eq. (7) does not hold. In what follows we therefore expect our results to agree with experiment for the range of fields for which Eq. (7) is valid.

Using temperatures up to 2300°K and fields up to 6.4×10^5 volts cm^{-1}, Phipps and his collaborators[4, 5] very accurately measured the emitted electron current from tungsten and tantalum and observed periodic deviations from the Schottky line. They found further that the amplitude of the deviations increases with the field. These results were recently verified by the precise work of Nottingham.[6] Both Phipps and Nottingham agree that within the limits of experimental error the locations of the maxima and minima are independent of the temperature. However, there is as yet some disagreement about the temperature dependence of the amplitude; Phipps and his co-workers observed that the amplitude decreases with increasing temperature, while Nottingham observed no temperature dependence.

Mott-Smith[7] suggested that the transmission coefficient might be periodic because of partial reflection of the electrons on the potential hill just outside the metal surface (Fig. 1), but the special fields and approximations which he used did not give the correct results, because he used a parabolic approximation to the potential (4) which is not valid over even a small fraction of the large range of fields used in the experiments.

In the present investigation the W. K. B. method is applied for the solution of the wave equation to the right of x_1. In order to obtain that solution of this equation which represents an outgoing (i.e., transmitted) wave on the right side of the barrier, "connection formulae" must be applied. It is customary to set up these "connection formulae" by replacing the actual potential in the neighborhood of turning points by straight lines. This procedure is valid, however, only if the coefficient of ψ (i.e., $W-V$) in the wave equation has a zero of first order at the turning point. In the present case $(W-V)$ has a zero of second order; to determine the "connection formulae" the actual potential is replaced by a parabola (instead of a straight line) in the neighborhood of the turning point. After "connection formulae" are obtained, it is possible to calculate both the transmission coefficient $D(F, W)$ and its summation over the electrons $\bar{D}(F)$, in an entirely straightforward manner.

It is to be pointed out that no arbitrary, adjustable parameters are introduced into the solution. For this reason, the rather good agreement with experiment which is obtained serves as another check of the fundamental assumptions involved in the modern theory of emission of electrons from metals.

According to Eq. (7), deviations from the Schottky line will be obtained if $\bar{D}(F)$ changes as F is changed. Leaving the Schottky slope out of consideration, the deviations are given by

$$\Delta \log i = \log i - \log i_0 = \log \bar{D}(F) - \log \bar{D}(0). \quad (8)$$

[4] R. L. E. Seifert and T. E. Phipps, Phys. Rev. **56**, 652 (1939).
[5] D. Turnbull and T. E. Phipps, Phys. Rev. **56**, 663 (1939).
[6] W. B. Nottingham, Phys. Rev. **57**, 935 (1940).
[7] H. M. Mott-Smith, Phys. Rev. **56**, 668 (1939) and personal communication. The authors were greatly aided in this research by communications and conversations with Professor Mott-Smith.

The problem of finding the deviations is thus reduced to finding $\bar{D}(F)$. This we now proceed to do.

II. The Method

We have the following Schroedinger equations for the wave function:

$$d^2\psi_I/dx^2+W\psi_I=0 \qquad x\leqslant x_1, \quad (9a)$$

$$d^2\psi_{II}/dx^2+(W-W_a+1/2x+x/2x_0^2)\psi=0 \qquad x>x_1. \quad (9b)$$

The solution of (9a) may be written down immediately

$$\psi_I=a_1\exp(iW^{\frac{1}{2}}x)+a_2\exp(-iW^{\frac{1}{2}}x) \quad x\leqslant x_1, \quad (10)$$

the two exponentials representing the incident and the reflected wave, respectively. Assuming for the moment that we can obtain a solution of (9b) valid in the neighborhood of x_1, we can determine the transmission coefficient by setting

$$\psi_I(x_1)=\psi_{II}(x_1)\,; \quad \psi_I'(x_1)=\psi_{II}'(x_1) \qquad (11)$$

and solving for

$$D(W, F)=1-|a_2/a_1|^2. \qquad (12)$$

Since the emitted electrons have a Maxwellian distribution, one then obtains the energy independent $\bar{D}(F)$ by summing (12) over all electron energies, using the Maxwell distribution.

Our problem is now to find that solution of (9b) valid in the neighborhood of x_1, which for $x\gg x_0$ has the form of a transmitted wave:

$$\psi_{II}\sim C\phi^{-\frac{1}{4}}\exp\left[i\int_{x_0}^{x}\phi^{\frac{1}{2}}dx\right]$$

We may write (9b) as

$$d^2\psi/dx^2+\phi\psi=0\,;$$
$$\phi=W-W_a+1/2x+x/2x_0^2=\epsilon+(x-x_0)^2/2xx_0^2, \qquad (13)$$

where $\epsilon=W-W_a+1/x_0$ is the height of the electron energy over the maximum of the potential barrier.

The asymptotic expansion of the desired solution near x_1 is of the form

$$\psi\sim b_1\phi^{-\frac{1}{4}}\exp\left[i\int_{x_0}^{x}\phi^{\frac{1}{2}}dx\right]+b_2\phi^{-\frac{1}{4}}\exp\left[-i\int_{x_0}^{x}\phi^{\frac{1}{2}}dx\right]. \qquad (14)$$

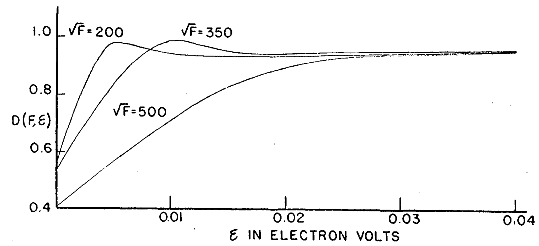

FIG. 2. The transmission coefficient (22) plotted as a function of the height of the electron energy above the maximum of the barrier for three different field strengths. The values of ϵ are given in electron volts; the values of F are in volts per cm.

The solution (14) represents a W. K. B. type of approximation for the wave function; it is certainly valid in regions where the potential is not a quickly varying function of x. However, we are interested in the validity of (13) near x_1 where the potential is a rather rapidly varying function, so we must use more precise validity arguments.

Now, because of the smallness of x_1, one may write the inequality $x_1/2x_0^2\ll 1/2x_1$, so that near x_1 the condition for the validity of the solution (14) is the same as the condition for the validity of the W. K. B. solution to the problem involving the pure image potential, for which $V=W_a-1/2x$. At x_1 this condition may be written in the form

$$\frac{W_a^3}{W^2}\left[1-\frac{5}{16}\frac{W_a}{W}\right]\ll 1.$$

It is seen that the condition is obeyed very well if $W_a\ll W$. However, it seems reasonable to believe that the principal contributions to the periodic deviations come from electrons whose energies are only slightly greater than W_a. If $W=W_a$, the left-hand side of the inequality is approximately one-half for tungsten, so that for these electrons the condition is not very well fulfilled. Nevertheless, we know that the exact solution of the Schroedinger equation with image potential for $W=W_a$ yields a transmission coefficient which differs from that obtained with the

W. K. B. solution by about 0.5 percent. Since we are interested in obtaining the transmission coefficient for a case which yields the same validity condition as the image case, it seems reasonable to expect that a solution of the type given by Eq. (14) will give a close approximation to the correct transmission coefficient. Consideration of higher order terms in the W. K. B. expansion would probably lead to a small correction to the nonperiodic term and a negligible contribution to the periodic term. We shall assume that the representation (14) will yield a transmission coefficient which is accurate enough to exhibit the deviations we are seeking.

III. Calculation of the Transmission Coefficient $D(F, W)$

Assuming (14), we shall determine the constants b_1 and b_2 and obtain the transmission coefficient $D(F, W)$ by the use of (11) and (12). The constants b_1 and b_2 are determined as follows: We expand the potential (4b) about the point x_0 and neglect terms of the third and higher orders. Thus,

$$V = W_a - 1/x_0 - (x-x_0)^2/2x_0^3.$$

If we put $z = (2/x_0^3)^{\frac{1}{4}}(x-x_0)$ and

$$\alpha = (x_0^3/2)^{\frac{1}{2}}(W - W_a + 1/x_0) = (x_0^3/2)^{\frac{1}{2}}\epsilon$$

the Schroedinger equation becomes

$$d^2\psi/dz^2 + (\alpha + z^2/4)\psi = 0. \tag{15}$$

This equation can be transformed into the differential equation of the parabolic cylinder in the following two ways:[8]

I. Let

$$u = ze^{i\pi/4}.$$

Then

$$d^2\psi/du^2 + (-i\alpha - u^2/4)\psi = 0.$$

We are interested in the asymptotic expansion for $x \ll x_0$, i.e., for $z \ll 0$; so we set $z' = ze^{i\pi}$. Then for[9] $z' \gg 0$

$$D_{-i\alpha-\frac{1}{2}}(z'e^{-3\pi i/4}) \sim z'^{-\frac{1}{2}}e^{3\pi i/8}e^{-3\pi\alpha/4}e^{-i(z'^2/4+\alpha\log z')} + \frac{(2\pi)^{\frac{1}{2}}e^{-i\pi/8}}{\Gamma(\frac{1}{2}+i\alpha)}e^{-\pi\alpha/4}z'^{-\frac{1}{2}}e^{i(z'^2/4+\alpha\log z')}. \tag{16}$$

II. Let

$$u = ze^{-i\pi/4}.$$

Proceeding as in I we have for $z' \gg 0$

$$D_{i\alpha-\frac{1}{2}}(z'e^{3\pi i/4}) \sim z'^{-\frac{1}{2}}e^{-3\pi i/8}e^{-3\pi\alpha/4}e^{i(z'^2/4+\alpha\log z')} + \frac{(2\pi)^{\frac{1}{2}}e^{i\pi/8}}{\Gamma(\frac{1}{2}-i\alpha)}e^{-\pi\alpha/4}z'^{-\frac{1}{2}}e^{-i(z'^2/4+\alpha\log z')}. \tag{17}$$

We associate

$$e^{i(z'^2/4+\alpha\log z')} \quad \text{with} \quad \exp\left[i\int_{x_0}^{x}\phi^{\frac{1}{2}}dx\right],$$

which means

$$e^{i(z^2/4+\alpha\log z)} \quad \text{with} \quad \exp\left[-i\int_{x_0}^{x}\phi^{\frac{1}{2}}dx\right].$$

The outgoing wave for $x \gg x_0$ should be of the form

$$\psi \sim c\exp\left[i\int_{x_0}^{x}\phi^{\frac{1}{2}}dx\right],$$

[8] The procedure used here of establishing the connection between the W. K. B. expansions for large and small x was first indicated by H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **58**, 225 ff. (1929). The procedure was extended to include zeros of orders higher than the second by S. Goldstein, Proc. London Math. Soc. **33**, 246 (1931–32), and by R. E. Langer, Bull. Am. Math. Soc. **XL**, 545 (1934). These authors, however, give the connection formulae in a form which is not applicable to our problem. The formulae developed here may be applied to the problem of the H^{2+} ion; they also give a complete solution to the problem advanced by E. C. Kemble, *Fundamental Principles of Quantum Mechanics* (McGraw-Hill, New York, 1937), pp. 109–112.

[9] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, third edition, 1920), pp. 348–349.

which is associated with $e^{-i(z^2/4+\alpha \log z)}$. It is to be noted that for the case $\epsilon=0$,

$$\phi^{\frac{1}{2}}=\begin{cases}(x_0-x)/\sqrt{2}x_0x^{\frac{1}{2}} & x<x_0\\ (x-x_0)/\sqrt{2}x_0x^{\frac{1}{2}} & x>x_0.\end{cases}$$

The solution under I possesses the asymptotic expansion for $z\gg 0$:

$$D_{-i\alpha-\frac{1}{2}}(ze^{i\pi/4})\sim z^{-\frac{1}{2}}e^{-i\pi/8}e^{\pi\alpha/4}e^{-i(z^2/4+\alpha \log z)},$$

which corresponds to

$$c\phi^{-\frac{1}{4}}\exp\left[i\int_{x_0}^{x}\phi^{\frac{1}{2}}dx\right],$$

the outgoing wave. Thus Eq. (16) gives the appropriate solution. Comparing (16) with (14), we have

$$b_1=e^{-i\pi/8}e^{-\pi\alpha/4}(2\pi)^{\frac{1}{2}}/\Gamma(\tfrac{1}{2}+i\alpha)\,;\quad b_2=e^{3\pi i/8}e^{-3\pi\alpha/4}.$$

Since $\Gamma(r)\Gamma(1-r)=\pi/\sin \pi r$, choosing $r=\frac{1}{2}+i\alpha$ we have

$$|\Gamma(\tfrac{1}{2}+i\alpha)|^2=\pi/\sin \pi(\tfrac{1}{2}+i\alpha)=2\pi/(e^{\pi\alpha}+e^{-\pi\alpha})\,;\quad |\Gamma(\tfrac{1}{2}+i\alpha)|=(2\pi)^{\frac{1}{2}}/(e^{\pi\alpha}+e^{-\pi\alpha})^{\frac{1}{2}},$$

so that we may write

$$b_1=\exp\left[-i\pi/8-i \arg \Gamma(\tfrac{1}{2}+i\alpha)\right]e^{-\pi\alpha/4}(e^{\pi\alpha}+e^{-\pi\alpha})^{\frac{1}{2}}.$$

Our solution in the neighborhood of x_1 is then

$$\psi\sim\exp\left[-i\pi/8-i \arg \Gamma(\tfrac{1}{2}+i\alpha)\right](e^{\pi\alpha}+e^{-\pi\alpha})^{\frac{1}{2}}e^{-\pi\alpha/4}\phi^{-\frac{1}{4}}\exp\left[i\int_{x_0}^{x}\phi^{\frac{1}{2}}dx\right]$$
$$+e^{3\pi i/8}e^{-3\pi\alpha/4}\phi^{-\frac{1}{4}}\exp\left[-i\int_{x_0}^{x}\phi^{\frac{1}{2}}dx\right],\quad (18)$$

an expansion which is valid at x_1 for all energies from the top of the barrier to infinity. However, the second term rapidly goes to zero for increasing electron energies; this means that as we consider electrons higher and higher above the barrier, the reflected current becomes smaller and smaller. Thus, with the use of the function of the parabolic cylinder we establish the connection between the asymptotic forms for large and small x. The validity of the W. K. B. type of approximation for this type of problem has been confirmed numerically. For the case when $F=0$, the Schroedinger equation may be solved exactly with the use of the confluent hypergeometric function. The transmission coefficients so obtained[10] are in close agreement with those obtained by the W. K. B. approximation to the exact solution.

We are now in a position to obtain the transmission coefficient $D(F, \epsilon)$.

$$D(F,\epsilon)=1-\left|\frac{a_2}{a_1}\right|^2=\left[1+e^{-2\pi\alpha}-\frac{\phi'}{4\phi^{\frac{3}{2}}}e^{-\pi\alpha}(1+e^{-2\pi\alpha})^{\frac{1}{2}}\left(1+\frac{\phi'^2}{64\phi^3}\right)^{\frac{1}{2}}\cos\left(v+\tan^{-1}\frac{\phi'}{8\phi^{\frac{3}{2}}}\right)\right.$$
$$\left.+\frac{1}{32}\frac{\phi'^2}{\phi^3}e^{-2\pi\alpha}+\frac{1}{64}\frac{\phi'^2}{\phi^3}\right]^{-1}$$

where

$$v=2\int_{x_0}^{x}\phi^{\frac{1}{2}}(x)dx-\arg \Gamma(\tfrac{1}{2}+i\alpha)\,;\quad \phi'=\left(\frac{d\phi}{dx}\right)_{x=x_1};\quad \phi=\phi(x_1).$$

[10] Exact calculations for this case have been made by L. A. McColl, Phys. Rev. **56**, 699 (1939); cf. also L. W. Nordheim, Proc. Roy. Soc. **121**, 626 (1928).

We may expand the transmission coefficient as follows:

$$D(F,\epsilon)=\frac{1}{1+e^{-2\pi\alpha}+y}\sim\frac{1}{1+e^{-2\pi\alpha}}-\frac{y}{(1+e^{-2\pi\alpha})^2}+\frac{y^2}{(1+e^{-2\pi\alpha})^3}.$$

Putting in the value for y and neglecting terms which are obviously of no consequence,

$$D(F,\epsilon)=\frac{1}{1+e^{-2\pi\alpha}}+\frac{\phi'}{4\phi^{\frac{3}{2}}}\frac{e^{-\pi\alpha}(1+\phi'^2/64\phi^3)^{\frac{1}{2}}}{(1+e^{-2\pi\alpha})^{\frac{3}{2}}}\cdot\cos\left(v+\tan^{-1}\frac{\phi'}{8\phi^{\frac{3}{2}}}\right)-\frac{\phi'^2}{64\phi^3}\cdot\frac{1}{(1+e^{-2\pi\alpha})^2}$$
$$+\frac{\phi'^2}{32\phi^3}\frac{e^{-2\pi\alpha}}{(1+e^{-2\pi\alpha})^2}\left(1+\frac{\phi'^2}{16\phi^3}\right)^{\frac{1}{2}}\cos\left(2v+\tan^{-1}\frac{\phi'}{4\phi^{\frac{3}{2}}}\right).\tag{20}$$

The coefficient of $\cos 2v$ is already very small when $\alpha=0$ and goes rapidly to zero as α is increased. Hence, only a very small error is introduced by neglecting this term. (Actually carrying through the summation including this term verifies this.) It is to be noted that terms involving the factor $e^{-\pi\alpha}=\exp\left[-\pi(x_0^3/2)^{\frac{1}{2}}\epsilon\right]$ may be neglected save for very small values of ϵ; hence, in these terms one may take

$$\frac{\phi'}{4\phi^{\frac{3}{2}}}=-\frac{1}{2x_1^2W^{\frac{3}{2}}}=-\frac{W_a^2}{2W^{\frac{3}{2}}}\sim\frac{(W_a)^{\frac{1}{2}}}{2}.$$

Because the exponential term goes to zero so rapidly, its contribution to the transmission coefficient is negligible if $\alpha>1$, the principal contribution coming for values of $\alpha\ll 1$. Hence, one may take

$$\arg\Gamma(\tfrac{1}{2}+i\alpha)\sim-(\gamma+2\log 2)\alpha$$

where γ is Euler's constant: $\gamma=0.5772$.

Writing

$$\int_{x_0}^{x_1}\phi^{\frac{1}{2}}(x,\epsilon)dx=\int_{x_0}^{x_1}\phi^{\frac{1}{2}}(x,0)dx+f(\epsilon)$$

and performing the integration of the left-hand member numerically, one sees that even for the largest ϵ values which need be considered (because of the factor $e^{-\pi\alpha}$ we need consider only very small ϵ values),

$$f(\epsilon)\ll\int_{x_0}^{x}\phi^{\frac{1}{2}}(x,0)dx;$$

furthermore, $f(\epsilon)$ goes rapidly to zero as $\epsilon\to 0$. Consequently, for the small ϵ values, $f(\epsilon)$ may be neglected. Thus

$$v=-4\sqrt{2}x_0^{\frac{1}{2}}/3+2/W_a^{\frac{1}{2}}+(\gamma+2\log 2)\alpha.\tag{21}$$

The error introduced here in the period of the deviations is negligible, but the error in the phase may be a few percent. With these simplifications (20) becomes

$$D(F,\epsilon)=\frac{1}{1+e^{-2\pi\alpha}}-\frac{W_a^{\frac{1}{2}}}{2}\frac{e^{-\pi\alpha}}{(1+e^{-2\pi\alpha})^{\frac{3}{2}}}\cos\left(v-\tan^{-1}\frac{W_a^{\frac{1}{2}}}{4}\right)-\frac{W_a^4}{16W^3}\frac{1}{(1+e^{-2\pi\alpha})^2}\tag{22}$$

with v given by (21). The transmission coefficient (22) is plotted in Fig. 2 as a function of the height of the electron energy above the barrier, for various values of the field intensity. The physical interpretation of the fluctuations in $D(F,\epsilon)$ is given in the discussion. We mention only that the positions of the maxima and minima of the fluctuations are determined by x_0, which is a measure of the width of the potential barrier, and by W_a which represents the height of the barrier.

IV. Summation over the Electron Energies

We shall now sum $D(F, \epsilon)$ over all electron energies and thus obtain the energy independent transmission coefficient $\bar{D}(F)$ which is a function only of the temperature, the height of the barrier, and the field. Since we are interested only in electrons for which $W > W_a$, the Maxwellian energy distribution may be used, one has

$$\bar{D}(F) = \frac{1}{kT} \int_0^\infty D(F, \epsilon) e^{-\epsilon/kT} d\epsilon.$$

In summing over all electron energies, the last term of (22) may be dropped; also

$$(1+e^{-2\pi\alpha})^{-\frac{3}{2}} \sim (1-\tfrac{1}{2}e^{-2\pi\alpha}) \sum_{n=0}^{\infty} (-1)^n e^{-2n\pi\alpha}.$$

Thus

$$\bar{D}(F) = \frac{1}{kT} \int_0^\infty \sum_{n=0}^{\infty} (-1)^n \exp\left[-\left\{2n\pi\left(\frac{x_0^3}{2}\right)^{\frac{1}{2}} + \frac{1}{kT}\right\}\epsilon\right] d\epsilon - \frac{W_a^{\frac{1}{2}}}{2kT} \int_0^\infty e^{-\pi\alpha}(1-\tfrac{1}{2}e^{-2\pi\alpha}) e^{-\epsilon/kT}$$

$$\times \sum_{n=0}^{\infty} (-1)^n e^{-2n\pi\alpha} \cos\left\{\frac{4\sqrt{2}}{3} x_0^{\frac{3}{2}} - \frac{2}{W_a^{\frac{1}{2}}} + \tan^{-1}\frac{W_a^{\frac{1}{2}}}{4} - (\gamma + 2\log 2)\alpha\right\}. \quad (23)$$

The integral of this expression can be readily carried through and leads to a complicated expression which, to a very good approximation, may be written as

$$\bar{D}(F) = 1 - \frac{\log 2}{2\pi\left(\frac{x_0^3}{2}\right)^{\frac{1}{2}} kT} - \frac{W_a^{\frac{1}{2}}}{2kT}\left[\left(\pi\left(\frac{x_0^3}{2}\right)^{\frac{1}{2}} + \frac{1}{kT}\right)^2 + (\gamma + 2\log 2)^2 \frac{x_0^3}{2}\right]^{-\frac{1}{2}}$$

$$\cdot \cos\left\{\frac{4\sqrt{2}}{3} x_0^{\frac{3}{2}} - \frac{2}{W_a^{\frac{1}{2}}} + \tan^{-1}\frac{W_a^{\frac{1}{2}}}{4} - \tan^{-1}\frac{\left(\gamma + 2\log 2\right)\left(\frac{x_0^3}{2}\right)^{\frac{1}{2}}}{\left(\pi\left(\frac{x_0^3}{2}\right)^{\frac{1}{2}} + \frac{1}{kT}\right)}\right\}. \quad (24)$$

The deviations from the Schottky line are then given by

$$\Delta \log i = \log \bar{D}(F) - \log \bar{D}(0). \quad (25)$$

It is probable that the integral of (23) does not yield a good value for the transmission when $F \rightarrow 0$. In the case $F = 0$ one may make a separate calculation of the transmission, a calculation which has been given by several authors. However, if one uses arbitrary intercepts in plotting the deviations, the deviations so obtained are independent of $\bar{D}(0)$. We are not interested in the case where F is different from zero but small, since there the periodic deviations are masked by "patch-effects."

V. Discussion of Results

According to Eq. (24) the transmission coefficient consists of two parts. The first term varies monotonically with the field, whereas the second term varies in a periodic manner as one changes the field. This periodic term may be interpreted physically as due to interference arising from the superposition of waves reflected from different heights on the potential hill, the different heights corresponding to different x-values.[11] For the

[11] The rectangular barrier serves as an example of reflection of the electron waves from two plane potential surfaces. In this case the interference of these two reflected waves yields a transmission coefficient which is strongly periodic in the energy of the incident particles. If one uses the rectangular barrier as an approximation to our barrier, assuming that changing the field alters the width and height of the barrier, one obtains a transmission coefficient strongly periodic in both the energy and the field. Reflec-

pure field potential (i.e., neglecting the image force), x_1 and x_0 coincide and no interference occurs. A potential involving no discontinuities which exhibits this interference phenomenon is, for instance, that given by Eckart.[12]

Using (24) one may easily calculate the positions of the maxima and minima of the deviations. These are shown in Table I along with the observed values;[3] it is seen that the agreement between theory and experiment is rather good. The positions of the maxima and minima are sensibly temperature independent. The period depends only upon x_0; i.e., it is the same for all metals. Physically this means that the period is determined by the image force and external force only and does not depend sensibly upon the exact shape of the potential near x_1. The amplitude, on the other hand, will depend somewhat more sensibly (as formula (24) shows) upon the shape (particularly the slope) of the potential near x_1. To illustrate this we may superpose a term b/x^2 on the potential; thus, $V(x) = W_a - 1/2x - b/x^2 - x/2x_0^2$. This potential probably changes the image potential more violently than is really

TABLE I. *Calculated and observed positions of the maxima and minima of the deviations in terms of x_0. The maxima are given in italics. The observed values are taken from the work of Turnbull and Phipps[5] and of Nottingham.[6] The values of x_0 are here given in angstrom units.*

Observed (Tungsten)		Calculated	
Nottingham	Turnbull and Phipps	W	Ta
	172.5±3.0	172.2	173.5
	146.0±2.2	*141.9*	*143.1*
$x_0 = 118.6$	118.6±1.4	114.5	115.6
94.9	*94.9±0.9*	*90.1*	*91.1*
74.2	71.4±0.6	68.6	69.4
54.6	*54.5±0.4*	*50.0*	*50.7*
37.6	37.6±0.3	34.3	34.9

tion from the rectangular barrier is analogous to the reflection of light at two surfaces where one has abrupt changes of the index of refraction. Reflection from the barrier of Fig. 1 is analogous to reflection of light in a medium with continuously varying index of refraction. The transmission coefficient obtained for the barrier of Fig. 1 differs in another essential respect from that obtained with the rectangular barrier; the periodic term does not disappear when the energy is just slightly under the barrier height, as it does in the case of the rectangular barrier. This is similar to the analogy between the transmission coefficients for the image potential and for the single step barrier. For the image potential the transmission is not zero when the energy is just below the height of the barrier; for the single step barrier $W = W_a$ yields a transmission zero.

[12] Carl Eckart, Phys. Rev. **35**, 1303 (1930).

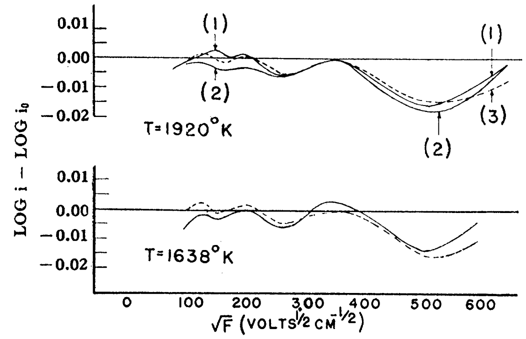

FIG. 3. Plots of the observed and calculated deviations for the two extremes of the temperature used by Turnbull and Phipps. The dotted curves represent the calculated values. As in the experiments, the intercepts are chosen arbitrarily.

the case. If b is chosen in such a way that the slope of the Schottky line is changed by only one percent, the period and phase of the deviations from the Schottky line are changed only slightly, whereas the amplitude may be changed by as much as twenty percent.

In addition to the experiments on the Schottky slope, another evidence for the validity of the image force at distances of 10^{-7} cm is here furnished by the good fit of the period of the deviations with experimental values. The check of amplitude and phase shows further that the chosen shape [Eq. (3)] is also a reasonably fair representation of the actual potential near x_1 (inasmuch as the dependency of the amplitude upon the slope of the potential is not critical). In principle, accurate conclusions could be drawn about the nature of the true potential from the comparison between theoretical dependency of the amplitude upon the shape of the potential near x_1 and the observed amplitude. Practically, however, this is not feasible; the concept of a fixed potential acting on the electrons and the one-dimensional treatment of the thermionic problem are, in all probability, good approximations, but their precise limitations are not known at present.

In Fig. 3, the dashed curves are obtained from (24); the solid curves are taken from the experiments.[5] As the table and the graph show, the agreement with experiment is good, inasmuch as no arbitrary parameters were introduced in our treatment. The W_i values used in the evaluation of (24) were obtained from the assumption of one free electron per atom. This assumption gives an upper limit for W_i; a smaller value of W_i, as indicated by M. F. Manning and M. I. Chodorov, Phys. Rev. **56**, 787 (1939), would improve the agreement with observation, as was pointed out to us by Dr. C. Herring. A smaller value of W_i also means an increase of x_1, which would be desirable for physical reasons.

From Eq. (24) it is seen that for low fields, i.e., for large x_0, the temperature dependence of the amplitude of the deviations is given approximately by the factor $1/kT$; however, this temperature dependence changes somewhat with the field. For all fields, the amplitude is increased by decreasing the temperature. This result is in agreement with the work of Phipps and collaborators, but is contrary to Nottingham's conclusion that the deviations are independent of temperature. However, this question is certainly unsettled from the experimental standpoint. From the theoretical viewpoint it is difficult to see how these deviations can be independent of temperature. It is hoped that further experimental work will clear up this issue.

The dependence of the deviations upon the barrier height, W_a, of the metal is worth pointing out. The principal change should occur in the shift of the maxima and minima due to the change in the phase term $-2/W_a^{\frac{1}{2}}+\tan^{-1}\frac{1}{4}W_a^{\frac{1}{2}}$. The barrier height which we have called W_a is the sum of the Fermi energy W_i and the work function χ. For tungsten one has $W_i=5.8$ ev and $\chi=4.53$ ev, so that $W_a=10.33$ ev or about 0.76 of our unit. For tantalum $W_i=5.2$ ev and $\chi=4.07$ ev, so that $W_a=9.27$ ev or about 0.68 of our unit. This difference is not enough to produce a great change in the positions of the extrema as one can see from Table I in which a comparison is made between the calculated positions of the extrema for tungsten and tantalum. Since no metal with a W_a value differing much from that of tungsten can be used for this work on thermionic emission, no data are available on the W_a dependence. However, it is hoped that the deviations will soon be obtained with photoelectron currents for metals with various values of W_a and for thermionic emission of thoriated metals.

As we pointed out in the introduction, our theory does not take into account any intense field emission. However, if the emitting metal surface is not perfectly smooth, certain small areas of it are subjected to fields larger than the apparent or average applied field which one records. Thus at fields of 4×10^5 volts cm^{-1} certain small areas of the emitting surface are subjected to fields of 10^6 volts cm^{-1} or greater, and electrons are pulled from these areas and tunnel through the potential barrier of Fig. 1. The current due to these electrons is small for fields of 4×10^5 volts cm^{-1}, but it is large enough to affect our small deviations at these fields. This fact explains the marked deviation (as shown by the curves of Fig. 2) of theory from experiment for fields higher than 3.5×10^5 volts cm^{-1}. It is very probable that one can use the parabolic connection to develop an expression for the transmission coefficient of the potential (4) valid for all electron energies. One would then obtain a theory taking all currents into account. However, the influence of any emission save thermionic field emission is so small with the fields used by the experimenters that the simplified theory presented here covers the experiments very well.

Part II of this paper, discussing the photoeffect in electric fields and the transition from thermionic to intense field emission, will appear in the near future.