Periodic Deviations in the Schottky Effect for Molybdenum*

E. G. BROCK,† A. L. HOUDE,‡ AND E. A. COOMES
University of Notre Dame, Notre Dame, Indiana
(Received October 2, 1952)

Periodic deviations in the Schottky effect for molybdenum have been measured over a field range of 10^4 to 10^5 volts cm^{-1} in a temperature range of 1400 to 1800°K. The results, interpreted in terms of the two reflection parameters λ and μ, justify the assumption of a mirror image barrier for the emitted electrons.

I. INTRODUCTION

PERIODIC deviations in the Schottky effect have been studied experimentally for tungsten,[1–3] tantalum,[2,4] and for tantalum contaminated with thorium.[4] A quantum-mechanical theory of electron emission[5–7] allows an interpretation of these studies in terms of the field dependence of the electron reflection coefficient for the potential barrier at the emitter surface. This analysis suggests the possibility of using Schottky plots as a tool to investigate some of the surface properties of solids.[8]
Such an investigation was undertaken in the case of tantalum,[4] and now has been continued for molybdenum.

Thermionic emission currents ranging from 10^{-5} to 10^{-9} amp were measured over a temperature interval of 1400 to 1800°K for molybdenum filaments. The periodic deviations in these currents were obtained over a field range of 10^4 to 3×10^5 volts cm^{-1}, and these results are related to the surface potential barrier through the two reflection parameters λ and μ suggested by Herring and Nichols.[8]

II. RESUME OF THEORY

Periodic deviations are related to the field dependent transmission coefficient through the relation[4,6]

$$F_2 = \text{the periodic part of } \log[\bar{D}(E)/\bar{D}(0)], \quad (1)$$

where F_2 is the periodic deviation, $\bar{D}$ is the transmission coefficient averaged over the energy distribution of the emitted electrons, and E the electric field applied to the emitter surface.

Guth and Mullin[7] obtained an expression for F_2 from the straightforward computation of $\bar{D}(E)$ for the one-dimensional box model. This barrier model has been plotted in Fig. 1 for the several applied fields of interest, to illustrate how its shape changes with field. The important mathematical relations derived for this model are listed in Fig. 1, and the general assumptions basic for these relations are: (a) the potential barrier to the left of x_1 is constant, and to the right of x_1 is due to the mirror image and applied fields; and (b) the potential barrier has a discontinuous slope at x_1. As a consequence of these assumptions the location of the barrier maximum, designated as x_0, depends only upon the applied field; theoretically, x_0 moves in toward x_1 from 601 to 19A as the applied field is increased from 10^3 to 10^6 volts cm^{-1}. Simultaneously the barrier half-width is decreased from 5.18×10^5 to 518A, but the barrier height is decreased only by 0.38 volt. The location of x_1 depends upon W_a alone; it is determined therefore for the particular emitter, but not affected by the applied field (see Fig. 1). For this model the Guth-Mullin expression for F_2 has been shown to be equivalent to[4]

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

where $E^{\frac{1}{2}}$ is designated by the symbol ξ. To a good approximation the C's are constants for a given emitter, and their computation as well as that of the f's involves only natural physical constants [see reference 4, Table I, and Eq. (5)]. The first cosine term results from electron reflections, while the second is due to tun-

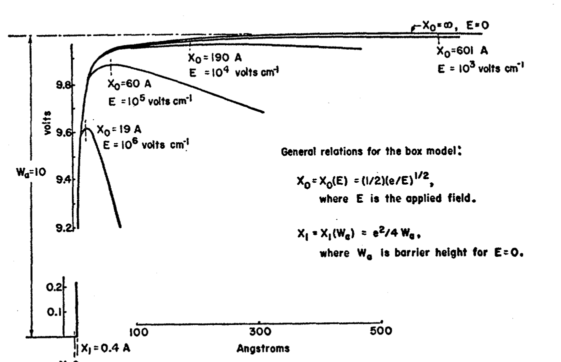

FIG. 1. The box model for an electron emitter with an electric field applied to its surface. $W_a=10$ volts is representative of the highly refractory metals. The periodic deviations in the Schottky effect are due to a large extent to the variations in the position of x_0 with applied field E.

* This research was sponsored by the U. S. Navy Bureau of Ships.
† Now at the General Electric Research Laboratory, Schenectady, New York.
‡ Now at St. John Fisher College, Rochester, New York.
[1] R. L. E. Seifert and T. E. Phipps, Phys. Rev. **53**, 493 (1938); **56**, 652 (1939).
[2] D. Turnbull and T. E. Phipps, Phys. Rev. **56**, 663 (1939).
[3] W. B. Nottingham, Phys. Rev. **57**, 935 (1940).
[4] Munick, LaBerge, and Coomes, Phys. Rev. **80**, 887 (1950).
[5] H. M. Mott-Smith, Phys. Rev. **56**, 668 (1939).
[6] E. Guth and C. J. Mullin, Phys. Rev. **59**, 575 (1941).
[7] E. Guth and C. J. Mullin, Phys. Rev. **61**, 339 (1942).
[8] C. Herring and M. H. Nichols, Revs. Modern Phys. **21**, 185 (1949), Chap. 4.

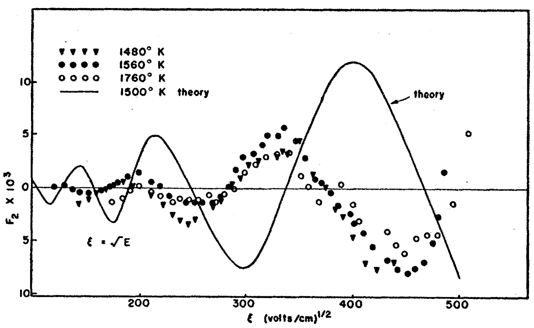

FIG. 2. Periodic deviations F_2 from the Schottky effect for clean molybdenum. The theoretical curve is calculated from the Guth-Mullin theory for $W_a = 10.2$ volts.

neling. Since both cosines have the same period, namely[9] $2\pi/C_3 = 2\pi/357.1$, they may be combined into the single term

$$F_2 = (C\xi^{3/2}/T)\cos[(357.1/\xi^{1/2}) + P], \qquad (2b)$$

where C and P are parameters identified as

$$C = C_2[(1/f_1)^2 + (1/f_2)^2 + (2/f_1 f_2)\cos(C_4 - C_5)]^{1/2},$$

$$P = \tan^{-1}\left[\frac{f_2 \sin C_4 + f_1 \sin C_5}{f_2 \cos C_4 + f_1 \cos C_5}\right].$$

The original C's and f's specified in Eq. (2a) were practically functions of W_a alone; this property may be transferred to the C and P of Eq. (2b).

The physical significance of the F_2-dependence on ξ and W_a in Eq. (2b) becomes clear when D is written to show how it includes the effect of interference between electrons reflected in the region x_0 with those reflected near x_1. Because x_0 is field-dependent, while the point x_1, as well as the shape of the potential near this point, are field-independent (see Fig. 1), Herring and Nichols[8] expressed D in terms of two partial reflection coefficients, as follows:

$$D = 1 - [|\mu|^2 + |\lambda|^2 + 2\,\mathrm{Re}(\lambda^* \mu)], \qquad (3)$$

where D is the over-all unaveraged transmission coefficient, λ is a complex quantity whose square gives the reflection coefficient for an electron at x_0, and μ is a similar complex quantity for x_1. The quantities D, λ, and μ are therefore functions of the electron energy; λ depends upon the applied field and therefore upon ξ, and μ is essentially independent of the applied field by definition. The periodic part of D comes from the last term on the right of Eq. (3), and F_2 is obtained by averaging this term over all electron energies. When a Maxwellian distribution for emitted electrons is assumed, the averaging introduces the $1/T$ into the final equation (2b), so that $\xi^{3/2}$ in the amplitude and $357.1/\xi^{1/2}$ in the argument of the cosine are introduced by λ, while C and P have their principal contributions from the real and imaginary parts of μ. Therefore, if one could obtain λ and μ separately from experimental data, one would have a description of the barrier at two positions, namely x_0 and x_1. The theory in its present form cannot be used to make a direct separation of λ and μ from experimental data. It is possible, however, to determine whether or not the field dependence introduced by λ is that of a mirror image potential, and whether the μ implied by the data corresponds to the reflections of electrons from the discontinuity at x_1 for the box model.

III. EXPERIMENTAL METHOD AND DATA

The experimental tube and measurements already have been reported in detail.[4] In the present experiment the test filaments were 0.003-inch molybdenum wire[10]

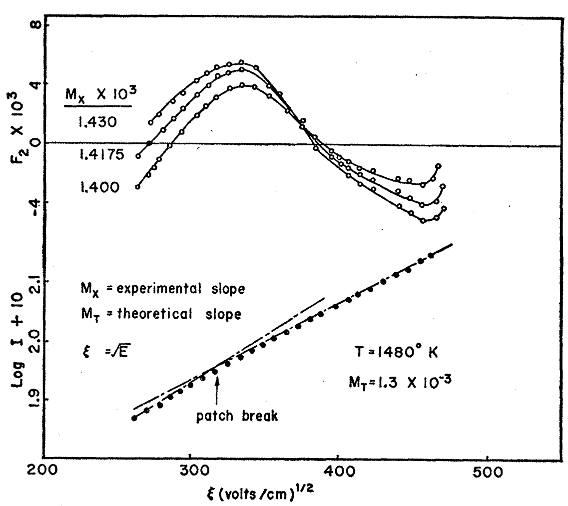

FIG. 3. The effect of choice of slope on the separation of periodic deviations F_2 from the Schottky plot in a patchy region of molybdenum. Note that the amplitude varies with slope, while there is little effect on the phase. The line drawn through the solid circles above the patch break has a slope of 1.4×10^{-3}; this is greater than the theoretical value computed from emitter temperature.

approximately 6.5 inches long. The diameter was determined by weighing and using 10.2 g cm^{-3} for the density.[11]

Prior to each set of emission measurements the molybdenum filament was flashed for two minutes at 2600°K. This seemed sufficient to clean the filament, for it brought the emission current to a value which was stable and reproducible to four significant figures over the two-hour period required in taking data for a precise Schottky plot.

[9] C_3 as given in reference 4 is slightly different from the value given here. Corrections have been made for more recent values of the physical constants.

[10] The molybdenum filament was obtained from the Fansteel Metallurgical Corporation, North Chicago, Illinois. Both unpolished and polished specimens of wire were tested, and the periodic deviations had identical patterns for both cases.

[11] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1949), thirty-first edition.

The filament temperature determinations were based on temperature-power data supplied by Moore and Allison of Bell Telephone Laboratories.[12] While the absolute temperature determined by these data is estimated to be correct to only $\pm 20°K$, constancy of temperature was checked during the taking of emission data by monitoring the filament heating current and voltage. The variation in temperature during a run was no greater than 1°K.

Precisions realized in the field and emission current measurements in the previous experiment[4] were reproduced here.

The Schottky plots obtained for clean molybdenum exhibited the modifications in slope due to the patch effect;[8] even at the highest fields the experimental slope was always greater than $(1.914/T)$ (cm volt^{-1})$^{\frac{1}{2}}$ predicted by Schottky theory, and in a few instances deviated by as much as 10 percent in the high field region. It was possible, however, as in the case of tantalum to separate each Schottky plot into several regions of constant slope and to obtain F_2-curves for molybdenum in the piecewise fashion previously described for tantalum.[4]

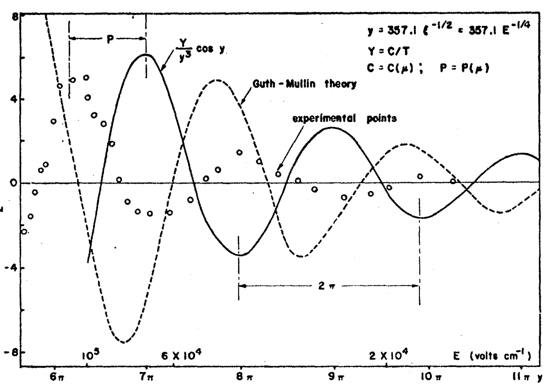

FIG. 4. F_2 *versus* y plot of periodic deviation theory. The curve has a constant period of 2π. A simple normalization to Y and a shift of P to the right should bring experimental points into coincidence with theory for $P=0$, if the emitter surface barrier follows the mirror image law. The Guth-Mullin theory for molybdenum is represented by the dashed curve. The experimental points are for molybdenum at 1480°K.

The experimental F_2-curves given in Fig. 2 are typical for clean molybdenum; here plots are given for temperatures of 1480, 1560, and 1760°K, respectively. An increase in amplitude with decrease in temperature may suggest itself, but the case is not clear as with tantalum.[4] The theoretical prediction that a change in temperature should not cause an appreciable phase change for the F_2 curves is verified. The phases were not appreciably sensitive to patch effects, while the amplitudes were affected to a large extent; Fig. 3 illustrates this (see reference 4, Fig. 4, for similar data in the case of tantalum).

[12] G. E. Moore and H. W. Allison (private communication).

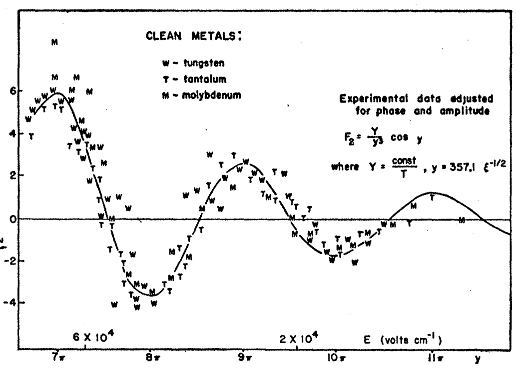

FIG. 5. Composite plot of F_2 *versus* y of periodic deviation data for the clean, highly refractory metals for a temperature range of 1200 to 2300 deg K, indicating that the surface potential barrier is mirror image.

IV. DISCUSSION OF RESULTS

The solid curve in Fig. 2 is a plot of the Guth-Mullin theory in which $W_a = W_i + e\phi = 5.8 + 4.4 = 10.2$ ev has been used for clean molybdenum. The comparison of experiment with theory reveals the same trends observed in all previous data for the clean highly refractory metals. The over-all form of the experimental curves follows the Guth-Mullin theory, with two important differences: (1) the experimental amplitudes are less than the theoretical, and (2) the extrema for the theoretical curves are shifted to larger values of ξ. While these differences may be attributed in a general way to patch effects and to the approximate character of the box model theory, particular and fundamental information seems available when an analysis based on the λ and μ coefficients is pursued.

As a first approximation, all of the field dependence of F_2 can be assumed to be due to λ because it is connected with x_0 alone. Thus, it is the mirror image λ that introduces specific analytic forms $\xi^{\frac{3}{2}}$ into the amplitude and $357.1/\xi^{\frac{1}{2}}$ into the argument of the cosine of Eq. (2) for the box model (the $1/T$ enters from averaging over the energy distribution of emitted electrons). That this field dependence peculiar to the mirror image barrier is verified may be clearly demonstrated if experimental data are compared with Eq. (2) transformed to

$$F_2 = (Y/y^3)\cos(y+P), \tag{4}$$

by letting $y = 357.1\xi^{-\frac{1}{2}}$, and $Y = (357.1)^3 C/T$. Equation (4) transforms F_2 to an oscillating function with a constant period of 2π. Figure 4 is a graphical illustration of this function; the solid curve is a plot of F_2 *versus* y for $P=0$ and Y arbitrary, while the dashed curve in this figure is a replot of the Guth-Mullin theory represented in Fig. 2 by the solid curve. Typical transformed experimental points (the 1480°K data from Fig. 2) are shown as open circles in Fig. 4. If these data are for a mirror image λ, normalization by a constant amplitude factor and a simple phase shift to the right should bring coincidence between experiment and the theoretical solid curve for $P=0$. This follows since Y and P are both independent of the field.

These two adjustments, namely the phase shift and the amplitude normalization, have been made for molybdenum, and also for the tungsten and tantalum data previously reported. A composite graphical representation together with the theory is given in Fig. 5. The adjustment factor for the amplitude varied between 1.5 and 2 for the three metals, after taking into account the $1/T$ variation; this range is not beyond the amplitude uncertainty due to the patch effect (see Fig. 3). Figure 5 represents the three highly refractory metals for an over-all temperature range from 1200 to 2300°K. Apparently the mirror image law is justified, and the λ part of the Guth-Mullin theory well verified.

It is apparent in Fig. 4 that the simple phase shift measures P in Eq. (4). In the instances of all data processed for Fig. 5, P had a different value for experiment than for the Guth-Mullin theory, and the deviation from the Guth-Mullin theory in every case was of the order of $\frac{1}{4}$ period. The inference is that the μ of the box model may not be completely justified.

The authors are grateful for the help received through discussions with others. In addition we acknowledge the technical assistance of Mr. Ernest Parsons and Mr. Fay Gifford in carrying out this experiment and in preparing the manuscript.

PHYSICAL REVIEW VOLUME 89, NUMBER 4 FEBRUARY 15, 1953

The Decay of Zn^{69}†

R. B. Duffield* and L. M. Langer‡
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico
(Received November 10, 1952)

The 52-minute ground state of Zn^{69} has been found to decay with a simple beta-spectrum of end point 0.897 ± 0.005 Mev. The 13.8-hour isomer of Zn^{69} decays to the ground state by emission of a gamma-ray of energy 0.436 ± 0.004 Mev. The conversion coefficient of this gamma-ray is 0.06 indicating a $M4$ transition.

INTRODUCTION

The 52-minute activity of Zn^{69} was first made by Livingood and Seaborg,[1] and absorption techniques showed the radiation to consist of beta-particles of energy 1 Mev[1,2] or subsequently 0.86 Mev.[3] No spectrometer measurements on this activity have been reported.

The 13.8-hour isomer of Zn^{69} has been shown to decay to the ground state by emission of gamma-radiation, the energy of which has been reported to be 0.439 and 0.450 Mev.[4] The internal conversion coefficient has been reported to be between 0.01 and 0.1.

Using a magnetic lens spectrometer we have examined the beta-spectrum of the 52-minute Zn^{69} and have measured the energy and the internal conversion coefficient of the gamma-ray accompanying the 13.8-hour isomeric transition. The beta-spectrum appeared to be simple and to have an end point of 0.897 ± 0.005 Mev. The gamma-ray energy was found to be 0.436 Mev and to have an internal conversion coefficient of 0.06.

† This work was performed under the auspices of the U. S. Atomic Energy Commission.
* Permanent address: University of Illinois, Urbana, Illinois.
‡ Permanent address: Indiana University, Bloomington, Indiana.
[1] J. J. Livingood and G. T. Seaborg, Phys. Rev. **55**, 457 (1939).
[2] Kennedy, Seaborg, and Segrè, Phys. Rev. **56**, 1095 (1939).
[3] E. Bleuler and W. Zünti, Helv. Phys. Acta **19**, 375 (1946).
[4] See, *Nuclear Data*, National Bureau of Standards Circular No. 499, for a summary.

EXPERIMENTAL PROCEDURE

The magnetic lens spectrometer used has been described in another paper.[5] A Geiger tube with a 3.6-mg/cm^2 mica window and a 0.5-inch diameter aperture served as detector. The resolution was 3 percent.

The sources were prepared by neutron irradiation of zinc in the thermal column of the Los Alamos homogeneous reactor. Zinc metal was evaporated in vacuum onto the desired backing material to form a source $\frac{3}{8}$ inches in diameter and perfectly uniform in thickness. This was then irradiated with thermal neutrons to form Zn^{69}. No interfering activities were found.

Data are given below for the beta-spectra from two different sources prepared in the above manner. The first had a thickness of 3.0 mg/cm^2 and was mounted on 0.00025-inch thick aluminum foil; the second had a thickness of 0.4 mg/cm^2 and was mounted on zapon of thickness approximately 50 micrograms per cm^2.

Sources of thicknesses 3 mg/cm^2 and 1 mg/cm^2 were used in the spectrometer for examination of the internal conversion electrons from the 13.8-hour isomeric transition.

The unconverted gamma-radiation was observed with a scintillation counter. A thallium-activated sodium iodide crystal 1 inch in diameter and 1 inch thick was used. The pulse-height distribution was

[5] L. M. Langer, Phys. Rev. **77**, 50 (1950).