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EFFECTIVE WORK FUNCTIONS OF DIFFERENT TYPES OF ELECTRON EMISSION FROM METALS

F. I. ITSKOVICH

Kharkov Military Engineering Institute

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It is shown that for an arbitrary electron energy distribution in metals the effective thermionic-emission and surface-photoeffect work functions, W_t and W_{ph}, reduced to zero field can exceed the true work function w, and can differ from each other as well as from the effective work function W_{fe} for field emission. In this case, with all quantities referring to the same single-crystal face, $W_{ph} \geq W_t \geq w$ and $W_{ph} \geq W_{fe} \geq w$. If the three reduced effective work functions are equal they are almost certainly identical with w. The thermionic current for an arbitrary energy distribution is also calculated. These results agree largely with experiment.

IT is well known that for many metals there are large discrepancies among the values of the work function that are determined from the contact potential difference and from different types of electronic emission. It is the aim of the present paper, together with an earlier paper,[1] to account for these differences. The basic circumstance in the case of a complex energy distribution is that the emitted electrons, as a general rule, possess a tangential (to the metal surface) momentum that is not close to zero. This means that a considerable portion of their energy cannot be used to surmount the potential barrier opposing their departure from the metal. The effective work functions of different types of emission are therefore generally greater than the true work function, whereas the contact potential difference is determined by the true work function independently of the dispersion law. The foregoing holds true, of course, subject to conservation of the tangential quasimomentum of an electron leaving a metal; this applies to single crystals whose surfaces are atomic planes (in which the Hamiltonian possesses translational symmetry). We shall henceforth consider samples of this kind.

Field emission was considered in [1]. In the present work we investigate thermionic emission and the threshold frequency of the surface photoeffect, and also compare the different effective work functions.

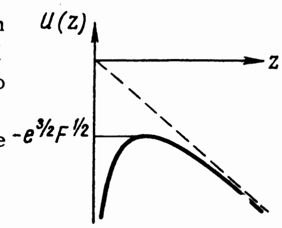

FIG. 1. Potential energy of an electron outside of a metal. Solid curve, taking the image force into account: $U(z) = -eFz - e^2/4z$, $e > 0$; dashed line, neglecting the image force: $U(z) = -eFz$. The metal fills the half-space $z < 0$.

1. THERMIONIC EMISSION

When the external electric field F is not excessively high, the emission current consists entirely of electrons that pass over the barrier (true thermionic emission). Then $E^{(z)} \geq -e^{3/2}F^{1/2}$, where $E^{(z)}$ is the energy of electron motion along the z axis, which is perpendicular to the metal surface, and $e^{3/2}F^{1/2}$ is the reduction of the barrier resulting from the image force (Fig. 1). We shall express $E^{(z)}$ in terms of two quantities that are conserved when an electron escapes from the metal—the energy E and the tangential quasimomentum **P** (the smallest of all equivalent values). The condition for electron escape from the metal then becomes

$$E - P^2/2m_0 \geqslant -e^{3/2}F^{1/2}, \quad v_z > 0,$$

where m_0 is the mass of a free electron and v_z is its velocity component. In other words, thermionic emission involves electrons which in the space of quasimomenta **p** are located on the part of the equal-energy surface[1)] that lies inside the cylinder $(p_x^2 + p_y^2)/2m_0 = E + e^{3/2}F^{1/2}$ with $v_z > 0$. Therefore the minimum energy E_{min} of thermionic electrons escaping from the metal is the lowest energy for which the projection $\Sigma(E)$ of the

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[1)] Here and henceforth we shall be considering an equal-energy surface with periodic repetition in **p** space.

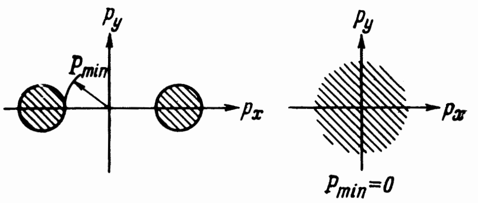


FIG. 2. Projection $\Sigma(E)$ of the equal-energy surface on the p_xp_y plane (shaded).

equal-energy surface on the p_xp_y plane has a common point with the circle $(p_x^2 + p_y^2)/2m_0 \leq E + e^{3/2}F^{1/2}$ [C(E)]. Obviously, $E_{min} \geq -e^{3/2}F^{1/2}$.

Using the notation (Fig. 2)

$$\min_{\Sigma(E)} P = P_{min}(E), \quad P_{min}^2(E)/2m_0 = \Delta(E),$$

we shall consider values of E_{min} in different cases (Fig. 3):

a) $\Sigma(-e^{3/2}F^{1/2})$ contains the coordinate origin $[\Delta(-e^{3/2}F^{1/2}) = 0]$, i.e., the p_z axis intersects the energy surface $E = -e^{3/2}F^{1/2}$. (This is the situation in the free electron model.) Then $E_{min} = -e^{3/2}F^{1/2}$.

b) $\Delta(-e^{3/2}F^{1/2} > 0$ and at some energy $E = E_g$ for which C does not touch the existing regions of Σ, new (elliptical, of course) regions of Σ appear inside C [because new electron groups (pockets) are created]. This occurs when

$$\Delta(E_g + 0) < E_g + e^{3/2}F^{1/2} < \Delta(E_g - 0); \tag{1}$$

in this case $E_{min} = E_g > -e^{3/2}F^{1/2}$.

c) $\Delta(-e^{3/2}F^{1/2}) > 0$ and regions of C and Σ are tangent for $E = E_{min}$. Then $E_{min} = -e^{3/2}F^{1/2} + \Delta(E_{min}) > -e^{3/2}F^{1/2}$.

Since a quite large number of bands usually overlap at energies above the barrier the most probable case is a).

The effective work function of thermionic emission is obviously the difference between E_{min} and the chemical potential of the electrons, which for the chosen energy normalization is negative and equal in absolute value to the work function w(T), where T is the emission temperature:

$$W_t(F, T) = w(T) + E_{min}(F) \geqslant w(T) - e^{3/2}F^{1/2}. \tag{2}$$

From a rigorous point of view E_{min} is somewhat dependent on the temperature because the dispersion law is temperature dependent. In case a) Eq. (2) becomes the same as for free electrons:

$$W_t(F, T) = w(T) - e^{3/2}F^{1/2}; \tag{2a}$$

the decrease of the effective work function in an electric field is known as the Schottky effect. In case b) we have

$$W_t(F, T) = w(T) + E_g > w(T) - e^{3/2}F^{1/2}, \tag{2b}$$

and the Schottky effect is absent (but only for values of F, allowed by the condition (1), when case b) does not pass over into case c). In case c) we have

$$W_t(F, T) = w(T) + \Delta(E_{min}(F)) - e^{3/2}F^{1/2} > w(T) - e^{3/2}F^{1/2}. \tag{2c}$$

After the reduction to zero field and zero temperature $[W_t(0, 0) = W_t$ and $w(0) = w]$, we obtain

$$W_t = w + E_{min}(0) \geqslant w; \tag{3}$$

$$W_t = w; \tag{3a}$$

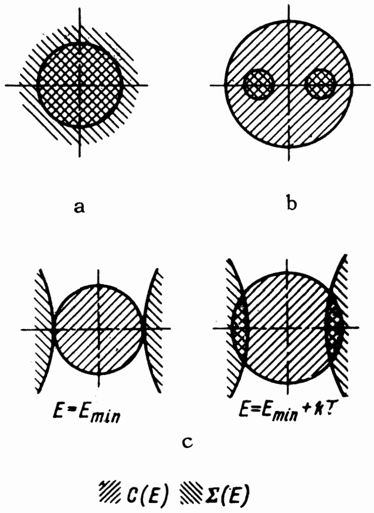
$$W_t = w + E_g, \quad E_g > 0; \tag{3b}$$

$$W_t = w + \Delta(E_{min}(0)),$$

$$E_{min}(0) = \Delta(E_{min}(0)) > 0. \tag{3c}$$

Thus the reduced effective thermionic work function equals w only when the energy surface $E = 0$ is intersected by the p_z axis; in the remaining cases $W_t > w$.

We shall now compare W_t with the effective work function W_{fe} of field emission. It was shown in [1] that $W_{fe} = w$ when the Fermi surface (from which extremely small cavities have been excluded) is intersected by the p_z axis; otherwise $W_{fe} > w$. However, the zero-energy surface is ordinarily considerably more highly developed than the Fermi surface, so that there is a greater probability that w will equal the reduced effective thermionic work function than that it will equal the effective field emission work function. Consequently, $W_{fe} \geq W_t$ occurs more frequently than the reverse. The available experimental data pertaining to a few faces of tungsten are in agreement


a b

c

FIG. 3. Different cases for the determination of E_{min} and the effective work function of thermionic emission.

with this statement. The newest data are to be found on p. 117 of [2], and in [3-8].

The thermionic current is calculated from the same initial equations as the field emission current.[1] If the wave functions, each consisting of one Bloch wave impinging on the metal surface, reflected waves decaying exponentially inside the metal, and outgoing waves, form an orthogonal system the emission current density is

$$j_z = -\frac{2e}{h^3}\sum_{s}\int_{(v_{zs}>0)} v_{zs}(\mathbf{p})D_s(\mathbf{p})f(\mathscr{E}_s(\mathbf{p}))\,d^3\mathbf{p}, \tag{4}$$

where $\mathscr{E}_s(\mathbf{p})$ is the distribution function for the s-th band, $v_{zs} = \partial\mathscr{E}_s/\partial p_z$, $D_s(\mathbf{p})$ is the transmission coefficient, and $f(E)$ is the Fermi distribution function. Conversion to the integration variables p_x, p_y, and E yields

$$j_z = -\frac{2e}{h^3}\int\Phi(E)f(E)\,dE, \qquad \Phi(E) = \int_{\Sigma(E)} D(E, \mathbf{P})\,d^2\mathbf{P}; \tag{5}$$

here

$$D(E, \mathbf{P}) = \sum_l D^{(l)}(E, \mathbf{P}),$$

where the summation is taken over all states with the same given values of E and **P**. The equations in (5) retain their validity in the general case of nonorthogonal wave functions, with the sole difference that $D(E, \mathbf{P})$ here denotes some quadratic form composed of the quantities $[D^{(l)}(E, \mathbf{P})]^{1/2}$ with a matrix that is determined by the reflection coefficients.

Since it would be impossible to determine the transmission and reflection coefficients exactly in any event, because the solution of a system of equations analogous to (4) in [1] would be required, we let $D \approx 1$ for $E^{(Z)} > -e^{3/2}F^{1/2}$ (for thermionic electrons having energies above the barrier) and $D = 0$ for $E^{(Z)} < -e^{3/2}F^{1/2}$. We then obtain

$$\begin{aligned} \Phi(E) &\approx S(E) \quad \text{for } E \geqslant E_{min}, \\ \Phi(E) &= 0 \quad \text{for } E \leqslant E_{min}, \end{aligned} \tag{6}$$

where S(E) is the area of the part of Σ(E) lying inside C(E);

$$j_z = -\frac{2e}{h^3}kT\Phi_t\exp\left\{-\frac{W_T(F, T)}{kT}\right\},$$

$$\Phi_t = \int_0^\infty \Phi(E_{min} + kTu)e^{-u}\,du \tag{7}$$

(with $W_t(F, T) \gg kT$). Obviously,[2)]

$$\Phi_T \sim \max_{0<u\lesssim 1} \Phi(E_{min} + kTu).$$

We shall now calculate Φ_T for the basic cases represented in Fig. 3:

a) $C(E) \subset \Sigma(E)$ for all energies making an important contribution to thermionic emission, i.e., for $0 < E + e^{3/2}F^{1/2} \lesssim kT$ (particularly, for free electrons); then $\Phi_T \approx 2\pi m_0 kT$.

b) The regions of Σ appearing inside C for $E = E_g$ retain their elliptical shapes and belong to the circle C(E) for $0 < E - E_g \lesssim kT$ with $\tilde{E}_{min}$ is the energy at which C becomes tangent with previously existing regions of Σ). In this case $\Phi_T \approx 2\pi nmkT$, where n is the number of ellipses and $m = (m_1m_2)^{1/2}$ is the effective mass of these ellipses.

c) The common portion of C and Σ, which become contiguous for $E = E_{min}$, remains small for $0 < E - E_{min} \lesssim kT$; here $\Phi_T \sim T^{3/2}$.

Thus both the exponential and the preexponential factor in (7) for the thermionic current can differ greatly from the values derived in the free electron theory.

2. THRESHOLD FREQUENCY OF THE SURFACE PHOTOEFFECT

We shall assume, as previously, that the electric field is not extremely high, so that the photoelectric current consists only of electrons having energies higher than the barrier. Let an electron in a state (E, **P**) on a metal surface absorb a photon, thus being raised to a state (E′, **P**′). This transition is accompanied by conservation of energy and of the tangential quasimomentum,[3)] while neglecting the momentum of the photon and assum-

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[2)] We exclude the case where $S(E_{min} + kTu) = 0$ for $\mu_1 \leqslant \mu \leqslant \mu_2$ and $u_1 \ll 1$. In this case $\Phi_T = \Phi_T^{(1)} + \Phi^{(2)}$, where

$$\Phi_T^{(1)} = \int_0^{u_1}\Phi(E_{min} + kTu)e^{-u}\,du \sim u_1 \max_{0<u<u_1}\Phi(E_{min} + kTu),$$

$$\Phi_T^{(2)} = \int_{u_2}^{\infty}\Phi(E_{min} + kTu)e^{-u}\,du,$$

and, correspondingly, $j_z = j_z^{(1)} + j_z^{(2)}$. The term $j_z^{(2)}$ actually corresponds to an effective work function $W_t(F,T) + kTu_2$ exceeding $W_t(F,T)$, although the latter will be the principal term for sufficiently small u_1.

[3)] When an electron in the interior of a metal absorbs a photon p_z is also conserved. This elevates the threshold frequency of the volume photoeffect over that of the surface effect.[9]

ing $\mathbf{P}' = \mathbf{P}$ so that the point $\mathbf{P}$ will belong simultaneously to $\Sigma(E)$ and to $\Sigma(E')$. An electron that has absorbed a photon will leave the metal if[4]

$$E' - P^2/2m_0 \geqslant -e^{3/2}F^{1/2}$$

[i.e., the point $\mathbf{P}$ is also in the circle $C(E')$], which is possible when

$$E' \geqslant E_{min}, \qquad E' \geqslant \Delta(E) - e^{3/2}F^{1/2}. \tag{8}$$

The effective work function of photoelectronic emission, determining the threshold frequency of the surface photoeffect, is the smallest value of the difference $E' - E$, where E' and E pertain to the same value of $\mathbf{P}$ and satisfy the aforementioned requirements:

$$W_{\text{ph}}(F) = \min_{\mathbf{P}} [E'(\mathbf{P}) - E(\mathbf{P})]; \tag{9}$$

here $E'(\mathbf{P})$ is the lowest energy for which $\mathbf{P}$ belongs simultaneously to Σ and the circle C:

$$E'(\mathbf{P}) = \min_{s,\, p_z} \mathscr{E}_s(\mathbf{P}, p_z) \quad \text{for}$$

$$\mathscr{E}_s(\mathbf{P}, p_z) \geqslant P^2/2m_0 - e^{3/2}F^{1/2};$$

$E(\mathbf{P})$ is the maximum energy of all states with a given value of $\mathbf{P}$ that are occupied by electrons at $T = 0$:

$$E(\mathbf{P}) = \max_{s,\, p_z} \mathscr{E}_s(\mathbf{P}, p_z) \quad \text{for} \quad \mathscr{E}_s(\mathbf{P}, p_z) \leqslant -w.$$

It follows from the inequality $E(\mathbf{P}) \leq -w$ and (8) that

$$\min_{\mathbf{P}} [E'(\mathbf{P}) - E(\mathbf{P})] \geqslant E_{min}(F) + w,$$

$$\min_{\mathbf{P}} [E'(\mathbf{P}) - E(\mathbf{P})] \geqslant \min_{E \leqslant -w} [\Delta(E) - E] - e^{3/2}F^{1/2},$$

so that[5]

$$W_{\text{ph}}(F) \geqslant W_{\text{t}}(F, 0), \quad W_{\text{ph}}(F) \geqslant W_{\text{fe}} - e^{3/2}F^{1/2} \tag{10}$$

[see (2) of the present work and (20) of [1]]; 'in zero field [$W_{\text{ph}}(0) = W_{\text{ph}}$] we will have

$$W_{\text{ph}} \geqslant W_{\text{t}}, \quad W_{\text{ph}} \geqslant W_{\text{fe}}. \tag{11}$$

We then have $W_{\text{ph}}(F) = W_{\text{t}}(F, 0)$ when

$$\mathbf{P}_{min}(E_{min} + 0) \in \Sigma(-w), \tag{12}$$

and $W_{\text{ph}} = W_{\text{fe}} - e^{3/2}F^{1/2}$ when

$$\mathbf{P}_{min}(E_M) \in \Sigma(\Delta(E_M) - e^{3/2}F^{1/2}), \tag{13}$$

where E_M is defined by[1]

$$-W_{\text{fe}} = \max_{E \leqslant -w} [E - \Delta(E)] = E_M - \Delta(E_M) \tag{14}$$

If both equalities exist simultaneously:

$$W_{\text{ph}}(F) = W_{\text{t}}(F, 0) = W_{\text{fe}} - e^{3/2}F^{1/2}, \tag{15}$$

then, as will be shown in the Appendix, $E_M = -w$ and the points $\mathbf{P}_{\text{min}}(E_{\text{min}} + 0)$ and $\mathbf{P}_{\text{min}}(-w)$ coincide. This last case is extremely unlikely except if $\mathbf{P}_{\text{min}}(E_{\text{min}} + 0) = \mathbf{P}_{\text{min}}(-w) = 0$, i.e., $W_{\text{fe}} = w$ and $W_{\text{ph}}(F) = W_{\text{t}}(F, 0) = w - e^{3/2}F^{1/2}$. Thus, if the reduced effective work functions for all three types of emission are identical, then they are almost surely equal to the true work function.

The paucity of experimental data on the work functions of single crystals limits the possibility of testing the derived relations. We shall compare data in [2] (p. 117), [3-5], [10] (p. 100), and [11]. For the (001) face of silver $W_{\text{ph}} = 4.81$ eV and $w = 4.62$ eV. For the (013) face of tungsten $W_{\text{ph}} \approx W_{\text{fe}}$, while for the (112) face W_{ph} is 0.15–0.38 eV smaller than $W_{\text{t}}(0, T)$ and W_{fe}.[6] This last case conflicts with the theoretical inequalities, but the investigators who supplied the data stated that their values of W_{ph} are unreliable because the faces of their sample were unstable during the measurements.

The different effective work functions of polycrystals were not averaged over crystal faces in a single identical manner; therefore our derived relations may remain unfulfilled (especially if the compared values pertain to different samples). It should also be remembered that the available values of the thermionic work function were not reduced to zero temperature. Nevertheless, in almost all cases where the differences between the work functions determined by different means are sufficiently large to establish inequalities reliably, the latter will each have the "correct" sense: $W_{\text{ph}} \geq W_{\text{t}} \geq w$, $W_{\text{ph}} \geq W_{\text{fe}} \geq w$. The accompanying table gives all available data, which were obtained from [2] (p. 94), [5], [10] (pp. 94–99), and [11-14].

For the purpose of any serious quantitative test of our present results, we would require measurements of the true and different effective work functions pertaining to the various faces of single-

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[4] Collisions of excited electrons may be neglected in the surface photoeffect.

[5] In the presence of anomalously small groups, which in thermionic or field emission are overwhelmed by larger groups with larger effective work functions (see footnote[2]) of the present work and footnotes[5] and [6] of[1]), $W_{\text{t}}(F,0)$ and W_{fe} in these equations can be understood to be smaller values belonging to the small groups. Or, retaining for $W_{\text{t}}(F,0)$ and W_{fe} the meaning that they are the actually observed quantities belonging to the large groups, $W_{\text{ph}}(F)$ can be understood as a quantity determining a second threshold frequency of the surface photoeffect at which the photocurrent begins to rise steeply.

[6] However, Hutson gives $W_{\text{t}}(0, 2000°\text{K}) = W_{\text{ph}}$.[4]

Work functions of polycrystalline metals

Metal	w, eV	$W_t(0, T)$, eV	W_{fe}, eV	W_{ph}, eV
Ag	4.29±0.02; 4.30±0.02 4.32±0.03; 4.44±0,01	4,8	—	—
Al	4,19±0.03; 4.24±0,03	—	—	4.39
Ba	2,35; 2.66; 2.42±0.05	2,3±0,01	2.45	2,48; 2.49; 2,51
Cr	—	4.60	—	4.37
Cs	1.84±0,01	1.8	1,92	—
Fe	4.16±0.02	4.21±0,05 * 4,48±0,06 **	—	4,63
K	—	—	2,18	2,26
Mg	3,61	—	—	3,60; 3.67; 3,68; 3,79
Mo	4.20±0,03; 4.21±0.04	4,17; 4,33; 4,20±0,02; 4,37±0,02	—	4.12; 4,35
Ni	4,73±0.03	4,61±0,05	—	4,87
Pt	—	5,32	—	6,2; >6,2
Ta	4,22±0.02	4,10; 4,19±0,02	—	4.05***; 4.3±0.1
U	3,19±0.01	3,27±0,05	—	—
Zn	4.11±0,03	—	—	4.24

*Above the β-γ transition point.

**Below the β-γ transition point.

***From work done in 1935 (see [10]).

crystal samples in the cases of metals whose electron spectra are sufficiently well known.

In conclusion I wish to thank I. M. Lifshitz, G. E. Zil'berman, and M. Ya. Azbel' for discussions of this work.

APPENDIX

If $W_{ph}(F) = W_t(F, 0) = W_{fe} - e^{3/2}F^{1/2}$ then (12) and (13) occur simultaneously. It follows from (12) that

$$P_{min}(-w) \leqslant P_{min}(E_{min} + 0),$$

i.e.,

$$\Delta(-w) \leqslant \Delta(E_{min} + 0), \qquad (\mathrm{I})$$

and in the case of equality the points $P_{min}(-w)$ and $P_{min}(E_{min} + 0)$ coincide. It follows from (13) that

$$\Delta(E_M) - e^{3/2}F^{1/2} \geqslant E_{min};$$

however, in all cases a)–c) we have

$$E_{min} \geqslant \Delta(E_{min} + 0) - e^{3/2}F^{1/2},$$

so that

$$\Delta(E_M) \geqslant \Delta(E_{min} + 0). \qquad (\mathrm{II})$$

From (I) and (II) we derive $\Delta(E_M) \geq \Delta(-w)$; on the other hand, $\Delta(E_M) \leq \Delta(-w)$, since

$$W_a = -E_M + \Delta(E_M) \leqslant w + \Delta(-w) \qquad (\mathrm{III})$$

[which is Eq. (21) of [1]], while $E_M \leq -w$. Therefore $\Delta(E_M) = \Delta(-w)$. From (III) we now obtain $E_M = -w$, and the substitution of this result in (I) and (II) yields $\Delta(-w) = \Delta(E_{min} + 0)$ along with coincidence of the points $P_{min}(-w)$ and $P_{min}(E_{min} + 0)$.

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