Field emission as a probe of the surface density of states

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Field-emission measurements of the total-energy distribution from a clean metal surface are shown to provide information about the density of states near the surface. Specifically, we find the field-emitted current per unit energy at energy ω to be given approximately by $j(\omega) \simeq (2\hbar/m)S\lambda^{-2}(\omega) \sum_m D_0^2(E_{\mathrm{T}}^m)$ $\times |\psi_m(x_m)|^2 \delta(\omega - \epsilon_m)$, where D_0^2 is the usual barrier-penetration probability with image potential corrections, $E_{\mathrm{T}}^m = \omega - \hbar^2 k_{\parallel}^2/2m$, where $k_{\parallel}$ is the electron momentum parallel to the surface, $|\psi_m(x_m)|$ is the amplitude of the metal electron at the classical turning point ($x_m \sim$ 1-2 Å), $\lambda(\omega)$ is a slowly varying function of ω, and S is the metal surface area. The D_0^2 factor in $j(\omega)$ strongly weights electron states with small $k_{\parallel}$ and consequently $j(\omega)$ measures the density of states at x_m arising from the component of the bulk band structure normal to the surface. Measurements of $j(\omega)$ for several single-crystal planes of tungsten will be presented and compared to the relevant photoemission data.

I. INTRODUCTION

It has been realized for some time, both theoretically[1-4] and experimentally,[5-9] that structure in the energy distribution of electrons field emitted through absorbed atoms or molecules can be used to characterize the electronic properties of the adsorbed species. What has generally not been appreciated is the potential ability of field emission to probe the electronic properties of the "clean" surface. This is a consequence of both a lack of properly presented experimental data and of clarity as to what the theory actually predicts.

Almost any total-energy distribution will have an exponential nature, decreasing rapidly with energy below the Fermi energy and being cut off at higher energies by the Fermi–Dirac distribution.[7,8] This exponential shape is a consequence of the field-induced barrier in the vacuum, which to first order (on a metal) is not affected by the electronic properties of the surface. This exponential tunneling probability must be divided out if the electronic properties of the substrate are to be investigated.[6] A fuller interpretation of the resultant curves is the subject of this paper.

Swanson and Bell[8] review the commonly accepted formulation of the field-emission tunneling problem, originating from Harrison's[10] WKB calculation. The conclusion of this calculation is that the energy distribution does not explicitly depend on the bulk density of states, but may be affected by the shape of the projection of a constant-energy surface on the transverse (to the surface) momentum plane. Calculations by Appelbaum and Brinkman[11] for tunnel junctions indicated the sensitivity of normal-metal tunneling to the electronic properties of the metal interface.

Plummer and Bell[6,7] have illustrated that total-energy distributions from clean single-crystal faces of tungsten contain structure presumably related to the surface density of states. This structure is sensitive to the surface condition and varies from plane to plane.[7] Likewise calculations by Duke and Faucher[4] for a one-dimensional Kronig–Penney model revealed structure in the energy distribution related to the one-dimensional band structure. They also found the energy distribution is sensitive to the position and magnitude of the δ function nearest the surface.

It is our objective in this paper to determine what property of the field emitter is measured by field emission. We will show that field emission provides a measure of the weighted density of states near the surface. This weighting factor strongly enhances the contributions of those electronic states with total momentum normal to the surface. More precisely, the field-emission current per unit energy at energy ω is approximately

$$j(\omega) \simeq (2\hbar/m)\, S\lambda^{-2}(\omega)$$

$$\times \sum_m D_0^2(E_{\mathrm{T}}^m)\, |\psi_m(x_m)|^2 \delta(\omega - \epsilon_m) \quad,$$

where the weighting factor D_0^2 is the usual barrier-penetration probability with image-potential corrections, $E_{\mathrm{T}}^m = \omega - \hbar^2 k_{\parallel}^2/2m$, where $k_{\parallel}$ is the electron momentum parallel to the surface, $\psi_m(x_m)$ is the metal wave function at the classical turning point x_m ($x_m \simeq$ 1-2 Å), $\lambda(\omega)$ is a slowly varying function of ω given by Eq. (30b), and S is the surface area.

The consequences of this result will be discussed, specifically under what conditions the "normal local density of states" at the surface can be measured. Field-emission measurements on single-crystal planes of tungsten[6] will be compared to photoemission data[12] where the one-dimensional density of states was purported to have been measured.

II. THEORY

In this section we calculate the field-emission current $j(\omega)$ at energy ω for a metal. The Hamiltonian for the metal plus external electric field is

$$H = T + V_m + V_f \quad , \tag{1}$$

where V_m is the metal potential and V_f is due to the external electric field. H is shown in Fig. 1. The metal is in the region of space $x < 0$ and the surface atoms are centered on the plane $x = 0$. The zero of energy is taken to be the vacuum level. For sufficiently large x,

$$V_m(\vec{r}) \rightarrow -e^2/4(x - D) \quad , \tag{2a}$$

$$V_f(\vec{r}) \rightarrow -eFx \quad , \tag{2b}$$

where D is the position of the image plane[13] and F is the strength of the external electric field. The Fowler–Nordheim calculation[14] of the field-emission current assumed

$$V_m(\vec{r}) = 0, \qquad x > 0 \tag{3a}$$

$$V_f(\vec{r}) = -eFx, \quad x > 0 \tag{3b}$$

and the standard expression for the field-emission current with image-potential corrections was derived[15] by assuming

$$V_m(\vec{r}) = -e^2/4x, \quad x > 0 \tag{4a}$$

$$V_f(\vec{r}) = -eFx, \qquad x > 0 \quad . \tag{4b}$$

In order to calculate $j(\omega)$ we use the Bardeen version[16] of the Oppenheimer-transfer-Hamiltonian approximation.[17] The validity of the transfer-Hamiltonian method as applied to field emission has been verified in some detail by Penn, Gomer, and Cohen.[3] It was shown that the transfer-Hamiltonian method gives the correct expression[14] for the field-emission current in the case that the po-
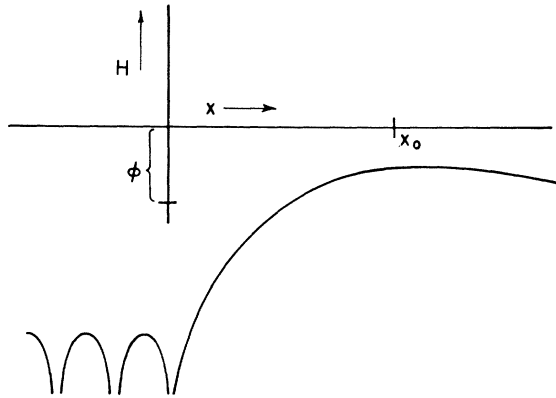

FIG. 1 Diagram of the metal potential and external-field potential entering H. The work function is ϕ and x_0 is the position at which the potential barrier is a maximum.

tentials are given in Eq. (3). Furthermore, the method gives essentially the correct expression for the field-emission current if a δ-function potential representing an adsorbate outside the metal is added to the potentials in Eq. (3). Define a "left-system" Hamiltonian by

$$H_L = T + V_m + V_f, \quad x < x_0 \tag{5a}$$

$$H_L = T + V_m, \qquad x > x_0 , \tag{5b}$$

where x_0 is the point at which $V_m + V_f$ is a maximum. The results of the calculation do not depend on the precise choice of x_0. H_L is shown in Fig. 2(a). A "right-system" Hamiltonian is defined by

$$H_R = T + V_f, \qquad x < x_0 \tag{6a}$$

$$H_R = T + V_f + V_m, \quad x > x_0 \quad . \tag{6b}$$

H_R is shown in Fig. 2(b). This choice of H_L and H_R ensures that if the metal is free-electron-like then the calculated tunneling current will be identical to that predicted by the WKB approximation.[15] The eigenfunctions and eigenvalues of H_L and H_R are denoted by ψ_L, E_L and ψ_R, E_R, respectively. At the energies of interest the eigenstates of H_L are largely confined to $x < 0$ and those of H_R to $x > 0$. Tunneling is viewed as transitions of electrons from eigenstates of H_L to those of H_R. The probability per unit time for an electron to tunnel from the eigenstate ψ_L to the eigenstate ψ_R is[3]

$$P_{L,R} = (2\pi/\hbar) \left| \langle \psi_L | \tau | \psi_R \rangle \right|^2 \delta(E_L - E_R) \quad , \tag{7a}$$

$$\tau = H - H_L \quad . \tag{7b}$$

The tunneling current per unit energy at energy ω is

$$j(\omega) = \sum_{L,R} f(E_L) P_{L,R} \, \delta(\omega - E_R) \quad , \tag{8}$$

where f is the Fermi function. In (7),

$$\tau = H - H_L = \theta(x - x_0) \, V_f$$

$$= \theta(x - x_0)(H_R - H_L) \quad , \tag{9}$$

where

$$\theta(x) = 1, \quad x > 0 \tag{10a}$$

$$\theta(x) = 0, \quad x < 0 \quad . \tag{10b}$$

Use of (9) in (7) yields[3]

$$P_{L,R} = (2\pi\hbar) \left| \langle \psi_L | J_{x_0} | \psi_R \rangle \right|^2 \delta(E_L - E_R) \quad , \tag{11a}$$

where

$$\langle \psi_L | J_{x_0} | \psi_R \rangle = (\hbar^2/2m) \int_{x_0} ds \left(\psi_L^* \frac{\partial}{\partial x} \psi_R - \psi_R \frac{\partial}{\partial x} \psi_L^* \right) .$$

$$\tag{11b}$$

The integral in (11b) is over the surface $x = x_0$.

In order to calculate $j(\omega)$ from (8) and (11) the eigenfunctions ψ_L, ψ_R must be obtained for $x \simeq x_0$.
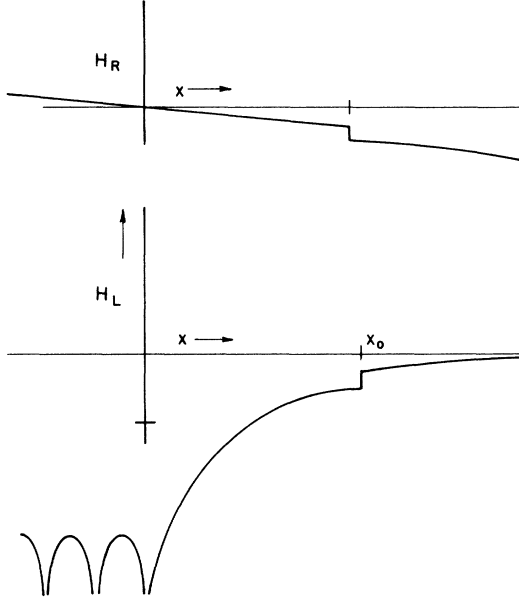
FIG. 2 (a) Potentials of the left system consisting of the metal potential and the external-field potential. The external-field potential of the left system is confined to $0 < x < x_0$. (b) Potential of the right system consisting of the external-field potential extended over all space and the metal potential confined to $x > x_0$.

For $x \simeq x_0$ the WKB approximation is valid and from (6)

$$\psi_R = N_R \, \kappa_R^{-1/2} \, exp \left[\int_{x_R}^{x} \kappa_R \, dx \right] e^{[i\vec{k}_\parallel^R \cdot \vec{\rho}]} \quad , \qquad (12a)$$

$$\kappa_R = \kappa_R(x, E_\perp^R)$$

$$= (2m/\hbar^2)^{1/2} (-eFx - E_\perp^R)^{1/2}, \qquad x < x_0 \quad (12b)$$

$$\kappa_R = (2m/\hbar^2)^{1/2}(V_m - eFx - E_\perp^R)^{1/2}, \quad x > x_0 \quad (12c)$$

$$E_R = E_\perp^R + (\hbar^2/2m)(k_\parallel^R)^2 \quad , \qquad (12d)$$

where x_R is the classical turning point for H_R and is obtained from the condition

$$E_\perp^R = V_m(x_R) - eFx_R \quad . \qquad (12e)$$

$N_R = N_R(E_\perp^R)$ is dictated by normalization and is conveniently obtained if $V_m - eFx$ is approximated by a square well of depth W for large x,

$$V_m - eFx \rightarrow - W, \quad x_R \ll W/eF \le x \quad . \qquad (13)$$

The final expression for $j(\omega)$ will be independent of W. Using (13),

$$\psi_R = 2N_R k^{-1/2} \cos$$

$$\times (\int_{x_R}^{x} k \, dx - \pi/4) e^{[i\vec{k}_\parallel^R \cdot \vec{\rho}]}, \quad W/eF \le x \qquad (14a)$$

where

$$k = (2m\hbar^2)^{1/2}(E_\perp^R + W)^{1/2} \quad . \qquad (14b)$$

The region $x > 0$ is assumed to be a cylinder of surface area S and length $L_f \gg W/eF$. Requiring ψ_R be normalized yields

$$N_R(E_\perp^R) = k^{1/2}/(2SL_f)^{1/2} \quad . \qquad (15)$$

In (12a) we have neglected a small term which represents a function that increases exponentially to the left for $x > x_0$. This term arises from the discontinuity in the potential at x_0 and has a magnitude of a factor of $\frac{1}{4} V_m(x_0)/E_\perp^R$ smaller than ψ_R at $x = x_0$. This term may be dropped since $E_\perp^R \sim \omega$ in the present calculations, and for field emission $|\omega| > \phi$, where ϕ is the work function of the metal. From (5) we find that for $x \simeq x_0$

$$\psi_L \propto N_L \kappa_L^{-1/2} \exp \left(- \int^x \kappa_L \, dx \right) e^{[i\vec{k}_\parallel^L \cdot \vec{\rho}]} \quad , \qquad (16a)$$

$$\kappa_L = \kappa_L(E^L; x)$$

$$= (2m/\hbar^2)^{1/2} (V_m - eFx - E_\perp^L)^{1/2}, \quad x < x_0 \quad (16b)$$

$$\kappa_L = (2m\hbar^2)^{1/2}(V_m - E_\perp^L)^{1/2}, \qquad x > x_0 \quad (16c)$$

$$E_L = E_\perp^L + (\hbar^2/2m)(k_\parallel^L)^2 \quad . \qquad (16d)$$

The integral in (16a) is indefinite. In order to complete the specification of ψ_L a lower limit to the integral, x_L, must be chosen. In order to make contact with the usual WKB treatment of tunneling it would be convenient to choose the lower limit to be the turning point of H_L. However, self-consistent calculations by Appelbaum and Hamann[18] for the (100) Na surface indicate that $V_m(\vec{r})$ has an appreciable dependence on the y, z coordinates for moderately large x. For Na, x_L is determined by $\phi = 2.7 \text{ eV} = eFx + | V_m(x_L, y, z) |$. For $eF = 0.3$ eV Å^{-1}, x_L varies from 2.2 to 2.7 Å depending on the values of y and z. The dependence of V_m on $\vec{\rho} = (y, z)$ for $x > x_L$ has been ignored by all previous authors and we will assume that for $x > x_L$, $V_m(\vec{r})$ is averaged over y, z to obtain a potential that depends only on x:

$$V_m(\vec{r}) \rightarrow V_m(x) = \int dy \, dz \, V_m(x, y, z), \quad x > x_L \quad (17a)$$

where x_L is determined by

$$E_\perp^L = V_m(x_L) - eFx_L \qquad (17b)$$

and it is understood that the averaged potential is used in (17b). Ignoring potential variations parallel to the surface will result in an image correction that has a small error. ψ_L is now given by

$$\psi_L = N_L \kappa_L^{-1/2} \exp \left(- \int_{x_L}^{x} \kappa_L \, dx \right) e^{[i\vec{k}_\parallel^L \cdot \vec{\rho}]} \quad , \qquad (18)$$

where κ_L is specified by (16b) and (16c), and V_m is understood to be the averaged potential. In (18) we have neglected a term which increases exponentially to the right for $x < x_0$. This term is a factor $\frac{1}{4}$

$eFx_0/|E_\perp^L|$ smaller than ψ_L at $x = x_0$.

Use of (12), and (18) in (11) yields

$$P_{L,R} = (2\pi/\hbar)\,[N_R N_L S\hbar^2/m\,]^2\,\Delta_{k_\parallel^L, k_\parallel^R}$$
$$\times D^2(E_\perp^L)\,\delta(E_\perp^L - E_\perp^R) \quad , \tag{19a}$$

$$D(E_\perp^L)^2 = \exp\left(-2\int_{x_L}^{x_R}\xi(x;E_\perp^L)\,dx\right) \quad , \tag{19b}$$

$$\xi(x;E_\perp^L) = (2m/\hbar^2)^{1/2}(V_m - eFx - E_\perp^L)^{1/2} \quad , \tag{19c}$$

where $\Delta_{k,k'}$ is a Kronecker Δ. Terms of order $[(V_m(x_0) - eFx_0)/E_\perp^L]P_{L,R}$ arising from $\partial\,\kappa^{-1/2}/\partial x$ have been neglected. Equation (19) is independent of x_0 and $D(E_\perp)^2$ is seen to be the usual WKB barrier-penetration probability since from (19a) $E_L = E_R$, and from (12e) and (17b) x_L and x_R are the two solutions of

$$E_\perp^R = E_\perp^L = V_m(x) - eFx \quad . \tag{20}$$

Use of (19) in (8) gives

$$j(\omega) = f(\omega)(2\pi/\hbar)(\hbar^2/m)^2 S^2 \sum_{L,E_\perp^R} N_L^2 N_R^2\,D^2(E_\perp^L)$$
$$\times \delta(E_\perp^L - E_\perp^R)\,\delta(\omega - E_L) \quad . \tag{21}$$

Carrying out the sum over $E_\perp^R$ and using (15) for N_R yields (22a)

$$j(\omega) = (S/\hbar)(\hbar^2/m)f(\omega)\sum_L N_L^2 D^2(E_\perp^L;p)\delta(\omega - E^L) \quad , \tag{22b}$$

where from (19b) and (19c)

$$D^2(E_\perp^L;p) = \exp\left\{-\left[\tfrac{4}{3}(2m/\hbar^2)^{1/2}(-E_\perp^L)^{3/2}/eF\right][1 - p]\right\}\cdot \tag{22c}$$

The quantity p depends on the exact form of $V_m(x)$. If $V_m = -e^2/4x$, then p is the usual image-potential correction[3] and is denoted by p_0. Replacing p by p_0 is a reasonable approximation since $p \sim p_0 \simeq 0.1$ for typical external fields F and because we are primarily interested in the ω dependence of $j(\omega)$ rather than its absolute magnitude. Thus the functional form of $D^2(E)$ is essentially independent of the properties of the field-emitting metal. On the other hand, N_L and E_L have only a weak dependence on F since they are determined by H_L. From (5), F enters H_L in the region $x < x$, however, V_f is zero in the metal and is dominated by V_m outside the metal except for $x \simeq x_0$, where $V_m \simeq V_f$. Thus N_L and E_L are essentially independent of F and depend on the properties of the metal as determined by $H_m = T + V_m$.

Therefore,

$$j(\omega) \simeq (2/\hbar)(\hbar^2/m)Sf(\omega)$$
$$\times \sum_m D_0^2(E_\perp^m)\,N_m^2\,\delta(\omega - \epsilon_m) \quad , \tag{23}$$

where a factor of 2 has been inserted to account for spin degeneracy and where $D_0(E_\perp^m) \equiv D(E_\perp^m;p_0)$. E_m is an eigenvalue of H_m, and N_m is determined by the condition that the eigenfunction ψ_m of H_m in the region $x \gg 0$ be

$$\psi_m = N_m \kappa_m^{-1/2}\exp\left(-\int_{x_m}^x \kappa_m\,dx\right)e\,(i\vec{k}_\parallel^m \cdot \vec{\rho}) \quad , \tag{24a}$$

$$\kappa_m = (2m/\hbar^2)^{1/2}\,(V_m - E_\perp^m)^{1/2} \quad , \tag{24b}$$

$$E_m = E_\perp^m + (\hbar^2/2m)(k_\parallel^m)^2 \quad , \tag{24c}$$

and x_m is given by

$$E_\perp^m = V_m(x_m) \quad . \tag{24d}$$

The quantity

$$\rho_m(\omega) = \sum_m \delta(\omega - \epsilon_m) \tag{25}$$

is the bulk density of states, and the presence of the surface has no effect in (25). $j(\omega)$ differs from $\rho_m(\omega)$ because of the factors D_0^2 and N_m^2. $D_0^2(E_\perp^m)$ is a very rapidly increasing function of $E_\perp^m$. The maximum value of $E_\perp^m$ is ω, in which case $k_\parallel^m = 0$. For $eF \simeq 0.3$ eV Å^{-1} and $\omega \simeq -5$ eV, $D_0^2(E_\perp^m) = \tfrac{1}{2}D_0^2(\omega)$ for $\omega - E_\perp^m \simeq 0.1$ eV. Thus, only those metal states with small $k_\parallel^m$ will contribute to $j(\omega)$. N_m can be a rapidly varying function of energy; however, it is instructive to examine the case where V_m is a square well (of depth V_0 in the metal) and is sufficiently slowly varying outside the metal that the WKB approximation is valid everywhere except near x_m. In that case

$$N_m^2 = k_\perp^m/2SL_m \quad , \tag{26a}$$

$$(k_\perp^m)^2 = (2m/\hbar^2)(E_\perp^m + V_0) \quad , \tag{26b}$$

$$E_m = (\hbar^2/2m)\,[(k_\perp^m)^2 + (k_\parallel^m)^2] \quad , \tag{26c}$$

where L_m and S are the length and surface area of the metal. Equation (23) becomes

$$J_0(\omega) = (2/\hbar)f(\omega)$$
$$\times \sum_{k_\parallel^m} D_0^2(\omega - \hbar^2(k_\parallel^m)^2/2m) \quad , \tag{27}$$

which is the standard result[15,19] for the field-emission current with image-potential corrections. Equation (27) for $j(\omega)$ contains almost no information about the bulk density of states and predicts a smooth $j(\omega)$. However, in a real metal the potential is periodic and (26a) is not correct. There can be structure in $j(\omega)$ although calculations indicate,[4,20] and our experiments show, that there is much less structure in $R(\omega) = j(\omega)/j_0(\omega)$ than in the bulk density of states.

A more physical interpretation of $j(\omega)$ can be arrived at as follows. In the region $x > x_m$ we approximate V_m by a linear function of x until x is sufficiently large that the WKB approximation is valid. This means

$$\kappa_m \to c(x - x_m)^{1/2} \quad , \quad x_m < x < x_{\text{WKB}} \tag{28}$$

where x_{WKB} is determined by the condition

$$\frac{d\kappa_m}{dx}\bigg/2\kappa_m^2 \ll 1 \tag{29}$$

and κ_m is given by (24b). For $V_m = -e^2/4x$ and $E_\perp^m$

$= -5$ eV, $x_m \simeq 0.8$ Å and $x_{WKB}^m \approx 1.5$ Å. At $x = x_m$, ψ_m is[21]

$$\psi_m(x_m) = \lambda_m N_m \qquad (30a)$$

and

$$\lambda_m = (\pi/3)^{1/2} (c/3)^{-1/3} [\Gamma(\tfrac{2}{3}) \cos(\pi/6)]^{-1} \quad , \qquad (30b)$$

where λ_m has a relatively weak dependence of $E_\perp^m$ through c; roughly $c \propto E_\perp^m$. Use of (30) in (23) yields

$$j(\omega) \simeq (2\hbar/m) S f(\omega) \lambda^{-2}(\omega)$$

$$\times \sum_m D_0^2(E_\perp^m) \, |\psi_m(x_m)|^2 \, \delta(\omega - \epsilon_m) \ . \qquad (31)$$

From (31) it is evident that $j(\omega)$ measures the metal density of states as the turning point weighted by a factor D_0^2, which restricts the sum over metal states to those with small $k_\parallel$. If only states with $k_\parallel = 0$ entered (31), $j(\omega)$ would measure the one-dimensional density of states at the turning point x_m. The result, Eq. (31), is not as rigorous as (23) primarily because (30a) overlooks the fact that the real-metal potential V_m is a function of y, z at $x = x_m$. Obviously at the very high fields used in the field-ion microscopy (10 times larger) the barrier is thin enough that the three-dimensional nature of the potential is critically important. In the field-emission case the barrier is very thick compared to the surface roughness on a single-crystal plane and Eq. (31) should be a good approximation. Clearly $j(\omega)$ can also be related to the density of states at any point $x > x_{WKB}$ via (24). Equation (23) for $j(\omega)$ can be simplified if $N_m = N_m(E_\perp^m, E_m)$ and $\rho_m^\perp = |\partial E_\perp^m / \partial k_\perp|^{-1}$ are much more slowly varying functions of $E_\perp^m$ than is $D_0(E_\perp^m)$. $D_0(E_\perp^m)$ is a very strongly increasing function of $E_\perp^m$ as discussed above. In this case

$$R \equiv j(\omega)/j_0(\omega)$$

$$= N_m^2(\omega, \omega) \rho_m^\perp(\omega) / N_0^2(\omega, \omega) \rho_0^\perp(\omega) \quad , \qquad (32)$$

where j_0 is the image-corrected Fowler–Nordheim current given by (27) and N_0 is the wave-function amplitde appropriate to a free-electron metal:

$$N_0^2(\omega, \omega) = (2m/\hbar^2)^{1/2}(\omega + V_0)^{1/2}/2 S L_m \quad ; \qquad (33)$$

$\rho_n^\perp$ and $\rho_0^\perp$ are the bulk densities of states for the real metal and the free-electron metal in the direction normal to the surface. Equation (32) predicts an $R(\omega)$ that is independent of external field F.

Equation (23) can be generalized to the case in which the metal electrons are interacting and may not be regarded as independent particles. The formalism developed by Appelbaum and Brinkman[11] leads to

$$j(\omega) \simeq (2\hbar/\pi m) S f(\omega)$$

$$\times \sum_m D_0^2(\omega - (\hbar^2/2m)(k_\parallel^m)^2) N_m^2 \operatorname{Im} G_{mm}(\omega) \quad , \qquad (34)$$

where $G(\omega)$ is the Green function of the metal. In the case that the electrons do not interact (34) reduces to (23).

III. EXPERIMENT

The objective of this section is to present experimental data to test the theory developed in Sec. II. The ideal test of the theory would consist of first calculating the band structure and wave functions at the surface for a real material, measuring the total-energy distribution of field-emitted electrons from this surface and then comparing the calculation and experiment via Eq. (23). Unfortunately, we are not yet at this stage of sophistication, but considering the nature of calculations like Appelbaum and Hamann's for Si surfaces,[22] there is evidence that this will soon be attained.

A more realistic approach will be pursued. The critical predictions of Sec. II will be identified and compared to experiment wherever possible. There are four general predictions which can be identified from Sec. II.

(i) Whenever there are metal-electron states with energy ω the shape of the energy distribution will be dominated by the tunneling probability $D^2(E_\perp^m)$.

(ii) There is weak structure in $j(\omega)$ induced by the electronic properties of the substrate [Eqs. (23) and (31)].

(iii) The total-energy distribution samples states with nearly zero transverse energy or momentum components [Eqs. (23) and (31)]. This predicts that the structure in the total-energy distribution $j(\omega)$ from a real material should be very sensitive to the normal direction of emission; i.e., the structure should be different for different single-crystal planes of the same material.

(iv) When the electronic properties of a given crystallographic direction, as represented by $\sum_m N_m^2 \delta(\omega - \epsilon_m)$ in Eq. (23), vary slowly with respect to the tunneling probabilities $D_0^2(E_\perp^m)$ as a function of transverse energy $E_\perp$, then the total energy distribution $j(\omega)$ samples the "one-dimensional" local density of states perpendicular to the surface [Eq. (31)]. This local density of states can be displayed experimentally by plotting the data in the form

$$R(\omega) = j(\omega)/j_0(\omega) \quad ,$$

where $j(\omega)$ is the measured energy distribution and $j_0(\omega)$ is a calculated free-electron distribution given by Eq. (27). This condition can be checked experimentally by measuring the field dependence of $R(\omega)$. $R(\omega)$ should be field independent [Eq. (32)] when $\sum_m N_m^2 \delta(\omega - \epsilon_m)$ is slowly varying over a 0.2-eV range in transverse energy.

If the $R(\omega)$ curves are not field independent then one or more of the following assumptions is not correct: (a) The potential is not correctly described by Eq. (4). The one-dimensional image potential may not adequately describe a real surface. (b) The band structure as described by $\sum_m N_m^2$ $\times \delta(\omega - \epsilon)$ in Eq. (32) is changing rapidly over a small change in transverse energy. (c) The transfer-Hamiltonian approximation to tunneling may be deficient.

Item (i) is obvious and predicted by all calculations. The reviews by Swanson and Bell[8] or Gadzuk and Plummer[7] illustrate this point. The experimental work of Plummer and Bell[6] and Gadzuk and Plummer[7] show that there is structure in the energy distribution $j(\omega)$ [Item (ii)] and that this structure is sensitive to the specific crystal plane or to the normal direction of emission [Item (iii)]. It is stated in the review by Gadzuk and Plummer[7] that the enhancement function $R(\omega)$ [Eq. (32)] is field independent [Item (iv)]. We illustrate that point now in Fig. 3. Figure 3 plots $R(\omega)$ for (100) W, which exhibits the most pronounced structure of any crystal plane of tungsten.[23,24] The $R(\omega)$ curves are arbitrarily normalized. $j_0(\omega)$ was calculated using 4.64 eV for the work function and the field determined from the shape of the Flower–Nordheim plot.

There is very little change in $R(\omega)$ as a function of field. The existing field dependence could result from changes in the electronic properties with transverse energy. As the field decreases $D_0(E_\perp^m)$
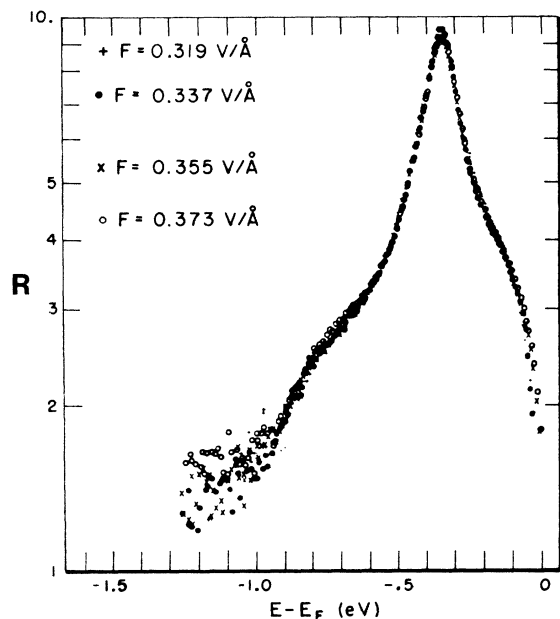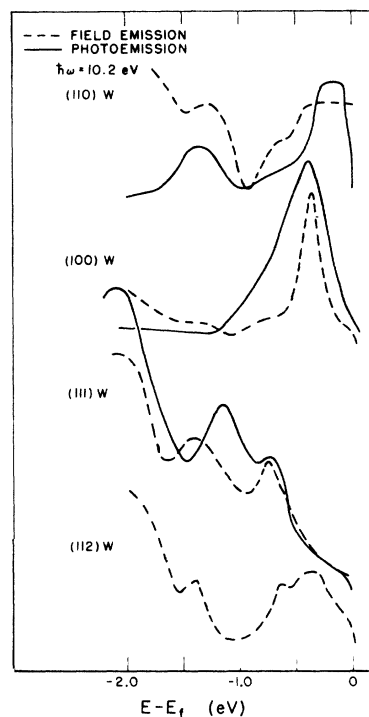

FIG. 4 Comparison of field-emission $R(\omega)$ curves with the photoemission energy distribution curves of Feuerbacher and Fitton (Ref. 12) for 10.2-eV photon excitation. Data from both techniques are shown for (100), (110), and (111) tungsten, and only field-emission data are shown for (112) W. Each of the field-emission curves is multiplied by an arbitrary normalization constant.

FIG. 3 $R(\omega)$ curves for (100) W for a range of electric fields from 0.319 to 0.373 V/Å.

becomes more sharply peaked at $E_\perp = 0$. On the other hand the field dependence could result from the field dependence of N_m^2. In itself Fig. 3 is not a sufficient test to prove that $R(\omega)$ is measuring the one-dimensional density of states normal to the (100) surface. It shows that changing the range of transverse energies being sampled (by changing the field) does not change $R(\omega)$. But in this small range of fields the change in transverse energy for which $D_0(E_\perp^m)$ falls by $1/e$ is only 0.050 eV, from 0.18 to 0.13 eV. Obviously in this model the extrapolation of $R(\omega)$ to $F = 0$ would give the one-dimensional density of states at the surface.

Incidentally, the field independence of $R(\omega)$ accounts for much of the variation in published values of the work function[5,23,25] obtained by combining the slopes of the Fowler–Nordheim and the energy distribution. Gadzuk and Plummer[7] demonstrated how the non-free-electron structure in the energy distribution displayed in the $R(\omega)$ curves invalidates the technique of Young and Clark.[26] If ϕ_0 is the real work function, S_{FN} the slope of the Fowler–Nordheim plot, V the applied voltage, and t and s slowly varying eliptical functions, then

Gadzuk and Plummer[7] showed that the measured work function ϕ_e using the Young-Clark[26] techniques would be

$$\frac{1}{\phi_e(V)} = \frac{1}{\phi_0} - \frac{2}{3}\left[\frac{\partial \ln R(\omega)}{\partial \omega}\right]\frac{Vs(y)}{S_{FN}\,t(y)} \quad .$$

Therefore ϕ_e will, in general, be incorrect and field dependent. The field independence of $R(\omega)$ can be utilized to extrapolate to an absolute work function. This is a subject of a forthcoming paper.

The capability for measuring the "one-dimensional" density of states at surfaces is the most important prediction of this theory, yet the one we can not directly test without detailed knowledge of the density of states at the surface. The only such information which exists is for (100) Si surfaces from the calculation of Appelbaum and Hamann[22] and there is no experimental data for this face at the present time. What does exist is the data of Feuerbacher and Fitton[12] for photoemission from (110), (100), and (111) W. Their contention is that they measure the one-dimensional density of states normal to the surface. Figure 4 shows the comparison of this data at $\hbar\omega = 10.2$ eV with the field-emission data for three planes. Most of the structure is the same, but the detailed shape cannot be compared because of the matrix-element effects in photoemission, which change the energy distribution with photon energy.

This comparison can in no way be construed as a test of our field-emission theory. The theory of field emission is on much better footing than photoemission, so what Fig. 4 suggests is that either (i) photoemission measures the local density of states of the surfaces or (ii) the density of states at the surface is nearly the same as the bulk and photoemission measures primarily the bulk density. Field emission with its limitations may play a crucial role in improving the understanding of photoemission.

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