Band-Structure Effects in the Field-Induced Tunneling of Electrons from Metals

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The theory of electron tunneling from metals into vacuum is investigated. Certain ambiguous conclusions reached in previous theoretical treatments are reconsidered. It is found that band-structure information is contained in the total energy distribution of field-emitted electrons. The problem of electron tunneling from narrow energy bands with a high density of states, well described in the tight-binding approximation, is treated. Expressions for the tunneling matrix element of electrons in tight-binding d bands tunneling to free-electron states outside the metal are obtained within the field-ionization approximation of Oppenheimer. Calculations are then given for the energy distribution of field-emitted electrons coming from a model of a real metal in which the band structure is a superposition of a free s-like band and a tight-binding d band. This is a reasonable qualitative model for the band structure of a noble metal. The relationship between the energy distribution and the band structure is established.

I. INTRODUCTION

THE theory of field emission of electrons from metals, as usually formulated, is applicable to free-electron metals,[1,2] interacting electron gases,[3] and superconductors,[3] structures with no static band effects. Attempts to include band-structure-type effects in expressions for the total energy distribution (TED) of field-induced tunneling electrons (field-emitted electrons) have appeared.[4–6] Frequently, band-structure effects are handled within the effective-mass approximation (EMA), still retaining a parabolic E versus k relation. Stratton has dealt with band effects which manifest themselves in radical departures from free-electron Fermi-surface shapes.[4] Itskovitch has considered the influences of Bragg reflections as well as Fermi-surface shapes to a limited extent.[5] BenDaniel and Duke have worked within the EMA in treating certain tunneling phenomenon.[6]

Harrison has presented a formulation of the tunneling problem in which certain band-structure effects are treated.[7] He shows that in his theoretical expression for the tunneling current, there is a "conspicuous absence of the density of states factor." But, as Harrison next points out, his conclusions are "a direct consequence of the resultant reciprocal relation between the particle velocity and the density of states." The problem is that such a reciprocal relation results from treating only the component of momentum normal to the barrier. The one-dimensional density of states is proportional to $(\partial E/\partial k_z)^{-1}$ and the particle-arrival rate is proportional to $\partial E/\partial k_z$, the product of the two being some constant. On the other hand, in a three-dimensional system, the density of states is given by

$$\rho = \int (\nabla_k E)^{-1} d\mathbf{S},$$

where the surface integral is done over a constant-energy surface. In this case, $v_z\rho$ does not equal a constant and thus, since the tunneling current is proportional to $v_z\rho$, some sort of density-of-states or band-curvature information should be obtainable from tunneling current characteristics.

Stratton[4] has given an expression for the tunneling current and TED from "a conductor of arbitrary band structure."[4] The expression given by Stratton is valid for arbitrary Fermi surface shapes but only within the spherically symmetric EMA, that is for conduction bands in which E is proportional to k^2.

It is felt that band-structure effects which might play an influencing role in the field-induced tunneling current can be placed in one of the following categories:

(1) different effective mass but still parabolic band shapes, treated by Stratton;

(2) effects arising from Fermi-surface topology, treated by Stratton[4] and also discussed by Swanson and Crouser[8];

(3) Bragg reflections at Brillouin-zone faces, treated by Itskovich[5];

(4) nearly flat bands such as tight-binding or d bands in which $\mathbf{k} \neq m\nabla_k E$, large density of states over a limited range of energies such as in transition metals, treated in this paper;

(5) tunneling matrix elements or probabilities much different depending on whether the tunneling electron comes from a free-electron-like s or p band or a tight-binding or d band, in which "conduction" occurs through hopping integrals, treated in this paper.

As noted above, the present paper is concerned mostly with the fourth and fifth effects. In Sec. II, a general expression for the tunneling current is derived along the lines followed by Stratton.[4] However, the assumption of a free-electron band structure is not invoked. The tunneling current and TED are then calculated for a model noble metal with the following approximate band structure. A single, wide, free-electron-like s band with a parabolic E versus k rela-

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[2] R. D. Young, Phys. Rev. **113**, 110 (1959).
[3] J. W. Gadzuk, Surface Sci. (to be published).
[4] R. Stratton, Phys. Rev. **135**, A794 (1964).
[5] F. I. Itskovich, Zh. Eksperim. i Teor. Fiz. **50**, 1425 (1966); **52** 1720 (1967) [English transls.: Soviet Phys.—JETP **23**, 945 (1966); **25**, 1143 (1967)].
[6] D. J. BenDaniel and C. B. Duke, Phys. Rev. **152**, 683 (1966).
[7] W. A. Harrison, Phys. Rev. **123**, 85 (1961).
[8] L. W. Swanson and L. C. Crouser, Phys. Rev. **163**, 622 (1967).

tion and a single, narrow d band cross and possibly hybridize to form some composite band structure. For many purposes, it is meaningful to view this band structure as the superposition of two independent bands.[9] The d band is approximated by $E=bk$, a reasonable first approximation to a tight-binding band with only nearest-neighbor-hopping integrals.[10] The resulting TED of field-emitted electrons is calculated in terms of the tunneling probabilities of electrons from s or d bands. In Sec. III, a description of tunneling from tight-binding bands is presented. Specific calculations for the tunneling matrix element between a d-band electron and free electrons are given. Within the context of this tunneling matrix element, numerical results for the TED from this model "noble metal" are given and it is then seen how one can go backwards from the TED to band-structure information. General conclusions, discussion, and hopes for the future appear in Sec. IV.

II. BAND-STRUCTURE EFFECTS

The traditional approach in field-emission theory is to write the expression for the TED of field-emitted electrons as a product of a supply or incident flux function $\equiv N(W,E)$ which may depend on the total energy of the particle and on the momentum (usually referred to as normal energy W) normal to the surface multiplied by the barrier-transmission probability$\equiv D(W)$, dependent on the normal energy and then integrated over all "normal energies" such that the total energy is a constant.[2] The TED is thus

$$\frac{dj}{dE}=\int_{W=E}^{-\infty} N(W,E)D(W)dW. \tag{1}$$

This result has also been obtained in a general many-body tunneling theory approach.[3] However, it is again unfortunate that the commonly used terminology has been adopted. The free interchange of vector momentum and directionally dependent energy can be easily effected only for simple systems such as a free-electron metal in which $E=ak^2$. In order to maintain generality, most quantum-mechanical calculations are usually carried out with respect to canonically conjugate variables, say position and momentum. However, in order to maintain some similarity with previous work, we shall try here to work with the "pseudo-canonically conjugate variables," position and energy. This actually is not too bad a problem when the information required from the dispersion relation is the value of energy at a given wave number. On the other hand, when density-of-states or group velocities, which depend upon the local slope of the E-versus-$\mathbf{k}$ relation, are needed, extreme care must be taken in passing from vector momentum to directionally dependent energy variables or important physics will be glossed over. Critical points in density-of-states functions and phase velocities rather than group velocities are examples of this.

At this point, we will rederive the TED with band-structure results of Stratton without introducing the parabolic band assumption. In analogy with Eq. (1) and Refs. 2 and 4, the number of field-emitted electrons with total energies between E and $E+dE$ is given by

$$\frac{dj}{dE}dE=2ef(E)\int^{E,E+dE} D(E,k_T,\varphi)v_z\frac{d^3k}{(2\pi)^3}, \tag{2}$$

where $f(E)$ is the Fermi function and v_z is the group velocity in the z direction of an electron with energy E and $\mathbf{k}$ vector $\mathbf{k}=\mathbf{k}_T+\mathbf{k}_z$, where $\mathbf{k}_T$ is the transverse component and $\mathbf{k}_z$ is the normal component to the surface. The transmission or tunneling probability D is, in general, a function of three dynamical variables. In the free-electron models, D depends only upon the normal component of momentum and thus "normal energy," a concept which is of vanishing utility in the three-dimensional case. Since we are considering tunneling of electrons at a given energy, the conserved quantity E should be one of the variables. Furthermore, the transverse $\mathbf{k}$ vector is usually assumed to be a conserved quantity in tunneling.[6] Thus, k_T and φ the angle of k_T in the plane of the surface are taken as the other variables. This choice of variables specifies the state of the tunneling electron. The group velocity in the z direction is written

$$v_z=(1/\hbar)(\partial E/\partial k_z).$$

Also, the differential volume element in k space between the energy surfaces E and $E+dE$ is

$$\int\int\int^{E,E+dE}\cdots d^3k\rightarrow dE\int\int\cdots\frac{d\mathbf{S}}{|\nabla_{\mathbf{k}}E|},$$

where the surface integral is done over the constant energy surface E. With these entries, Eq. (2) becomes

$$\frac{dj}{dE}=\frac{2ef(E)}{\hbar(2\pi)^3}\int\int D(E,k_T,\varphi)\frac{\partial E/\partial k_z}{|\nabla_{\mathbf{k}}E|}d\mathbf{S}. \tag{3}$$

If we define an angle θ' which is the angle between the vector $d\mathbf{S}$ and the z axis, then $d\mathbf{S}$ can be expressed in terms of its projection in the plane transverse to the k_z axis, call it ds, through $\cos\theta' d\mathbf{S}=d\mathbf{s}$. Conveniently, θ' also satisfies

$$\mathbf{z}\cdot\nabla_{\mathbf{k}}E=\cos\theta'|\nabla_{\mathbf{k}}E|=\partial E/\partial k_z.$$

Consequently, Eq. (3) assumes the more tractable form with $d\mathbf{s}=k_T dk_T d\varphi$:

$$\frac{dj}{dE}=\frac{2ef(E)}{\hbar(2\pi)^3}\int_0^{2\pi}d\varphi\int_0^{k_T^{\max}(E,\varphi)} D(E,k_T,\varphi)k_T dk_T. \tag{4}$$

[9] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. **152**, 505 (1966).

[10] J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964), p. 102.

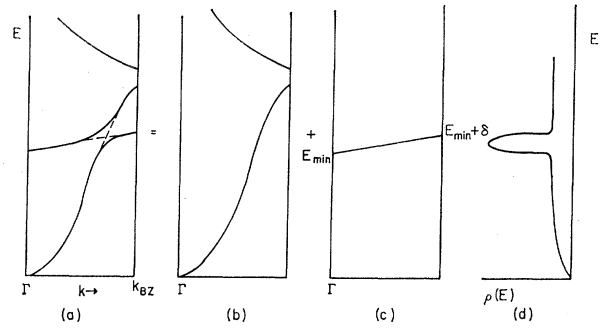

FIG. 1. Model band structure used in the calculations. (a) The complete structure formed by the independent bands of (b) and (c) crossing and hybridizing. (d) The resulting density-of-states function.

Equation (4) is still an exact result as we have not yet made any assumptions as to the functional form of the E-versus-$\mathbf{k}$ relation. The k_T integral can be written as a sum of a spherical energy surface term and a small correction integral which contains some of the information of the constant energy surface topology, somewhat related to the so-called "band-structure integral" of Stratton.[4] We obtain

$$\frac{dj}{dE}=\frac{ef(E)}{\hbar 2\pi^2}\left(\int_0^{k_T^{\max}(E)} D(E,k_T)k_T dk_T - \frac{1}{2\pi}\int_0^{2\pi} d\varphi \int_{\delta k_T(E,0)}^{\delta k_T(E,\varphi)} D(E,k_T,\varphi)k_T dk_T\right), \quad (5)$$

with $\delta k_T(E,\varphi)=k_T^{\max}(E)-k_T^{\max}(E,\varphi)$ the difference between the maximum transverse k vector of the shadow of the spherical and the true constant energy surface. The second integral will usually be much smaller than the first.

To continue in the spirit of past work, the k_T integration should be transformed to some sort of energy integral. This is not as straightforward as in the free-electron theories. Only in a free-electron metal does $E_T^{\rm FE}=\hbar^2k_T^2/2m$ or $k_Tdk_T=(m/\hbar^2)dE_T^{\rm FE}$, where the superscript FE refers to the fact that the particular energy is relevant only for a free-electron metal. In order to proceed, we now make two assumptions as to the nature of the energy bands, first that $E=f(|\mathbf{k}|)$, so that $\delta k_T(E,\varphi)=\delta k_T(E,0)$ and thus the second integral in Eq. (5) is zero. Second, we assume that E can be written as $E=f_1(k_z)g_1(E)+f_2(\mathbf{k}_T)g_2(E)$. This is always true if E is given by k raised to some power. As an example suppose a linear $E=bk$ relation. Since $k=k_z^2/(k_z^2+k_T^2)^{1/2}+k_T^2/(k_z^2+k_T^2)^{1/2}$ and $E=b(k_z^2+k_T^2)^{1/2}$, the separation in this case is possible. The total energy is often written as a sum of normal and transverse "energies" $E=W+E_T$ in the field-emission literature.[1–5,8] With the present separation scheme we can make the identification $W=f_1(k_z)g_1(E)$ and $E_T=f_2(k_T)\times g_2(E)$. Furthermore, we take $D(E,k_T)=D(E-E_T)=D(W)$.

With the preliminary remarks of the preceding paragraph we can write

$$k_Tdk_T=(m/\hbar^2)(dE_T^{\rm FE}/dW)dW,$$

realizing that the total energy is held constant. Since $dE=0=dW+dE_T$, we can substitute $dW=-dE_T$ and introduce the effects of transverse band curvature through

$$k_Tdk_T=\frac{m}{\hbar^2}\frac{dE_T^{\rm FE}}{dE_T}dE_T=\frac{m}{\hbar^2}\left(\frac{dE_T^{\rm FE}}{dk_T}\Big/\frac{dE_T}{dk_T}\right)dE_T.$$

Consequently Eq. (5) can be written as

$$\frac{dj}{dE}=Kf(E)\int_{E_{\min}}^{E} D(E-E_T)G(E_T)dE_T, \quad (6)$$

where $K=(me/2\pi^2\hbar^3)$, $G(E_T)=(dE_T^{\rm FE}/dk_T)/(dE_T/dk_T)$, and the limits of integration go from $E_{\min}=E(k=0)$ to E. Equation (6) can be rewritten as an integral on W:

$$\frac{dj}{dE}=Kf(E)\int_{E_{\min}}^{E} D(W)G(E-W)dW. \quad (7)$$

Equation (7) is the final expression with which to work. Note that G is in some senses the ratio of the real metal to free-electron metal two-dimensional density of states resulting from degeneracies in the transverse direction. If the real metal has a parabolic band and is thus free-electron-like, then there is no density-of-states information obtainable from the shape of the energy distribution as concluded by Harrison.[7] On the other hand, if we have unusual and interesting band structure departing radically from the free-electron model, then G will be dramatically different from unity. In this case the result of Eq. (7) shows that there is some sort of band-curvature information in the TED due to the presence of the "two-dimensional density-of-states factor."

To see how these ideas manifest themselves in numerical results, a simple model calculation is performed. Consider a theoretical noble metal in which the band structure consists of a single free-electron-like s band hybridized with a single narrow n-fold degenerate d band as shown in Fig. 1(a).[9] The basic components of this band structure are shown in Figs. 1(b) and 1(c) and the total density of states appears in Fig. 1(d). The point is that the true band structure can be envisioned as the sum of a parabolic and linear band. The parabolic band, with $E^s=a_1k^2$ and $a_1=\hbar^2/2m$, has a transverse structure $E_T^s=a_1k_T^2$. The narrow linear band of width δ, $E^d=E_0'+b_1'k$, has a transverse structure $E_T^d=b_1^2(k_T^2/E)$, where $b_1=\delta/k_{Bz}$, k_{Bz} is the k vector at the Brillouin-zone face in the direction of emission and thus in the transverse direction for a cubic crystal, and $E_{\min}$ is the energy for $k_T=0$ for a given total energy E.

The general point of view now is to calculate the TED twice, the first time for electrons tunneling from

a metal with the band structure of Fig. 1(b) and the second time for electrons tunneling from a pure tight-binding d-band metal with the Fig. 1(c) structure. The hypothesis is that the current from the theoretical noble metal with band structure shown in Fig. 1(a) is reasonably well approximated by the sum of the two nonhybridized bands.

First, the s-band contribution is determined. In this case, the tunneling probability $D_s(W)=e^{W/d}$, where $d\approx\hbar eF/2(2m\varphi)^{1/2}$, F is the applied field, and φ is the metal work function.[1,2] For the values of electric fields in field-emission experiments, $d\approx 0.1$–0.2 eV. For a pure free-electron s band, $G=1$ for all values of E. Thus the s-band TED takes the usual form

$$dj_s(E)/dE=j_s'(E)=(J_0/d)f(E)e^{E/d}, \tag{8}$$

with the Fermi-surface topology integral in Eq. (7) set equal to zero. J_0 is some function of the system parameters but not of energy. This of course is the usual free-electron result.

Next we must consider tunneling from the tight-binding d band. The writer was unable to find in the literature any treatments of tunneling from tight-binding bands. In Sec. III a model tunneling probability of electrons from d bands into the vacuum is calculated. For the time being we can characterize d-band tunneling by taking the tunneling probability $D_d(W)=e^{W/d}F(W)$, where $F(W)$ is a relatively slowly varying function of W whose magnitude is entirely unspecified at this point. However, $F(W)$ is calculated in Sec. III.

With the assumed d-band structure, $dE_T{}^d/dk_T=2b_1{}^2k_T/E$. Hence $G(E_T)=(\hbar^2k_{Bz}{}^2/2m\delta)(E/\delta)$ for $E_{\min}<E<E_0+\delta$ and $G=0$ otherwise. Consequently, the d-band TED becomes

$$j_d'(E)=(J_0/d)f(E)n\left(\frac{\hbar^2k_{Bz}{}^2}{2m\delta}\right)\frac{E}{\delta}\frac{1}{d}\int_{E_{\min}}^{E}e^{W/d}F(W)dW$$

for $E_{\min}<E<E_0+\delta$. Since $F(W)$ is slowly varying, it is set equal to $F(E)$, removed from the integral, and integrated to give

$$j_d'(E)=J_0f(E)(\hbar^2k_{Bz}{}^2/2m\delta)(En/\delta)\times(e^{E/d}-e^{E_{\min}/d}) \tag{9}$$

within the given limits on E. The complete TED is given by

$$j'(E)=j_s'(E)+j_d'(E)[\theta(E-E_{\min})-\theta(E-E_{\min}-\delta)]$$

with θ the usual step function. Using Eqs. (8) and (9),

$$\begin{aligned}j'(E)&=j_s'(E)\{1+(\hbar^2k_{Bz}{}^2/2m\delta)(nE/\delta)F(E)\\&\quad\times(1-e^{(E_{\min}-E)/d})\\&\quad\times[\theta(E-E_{\min})-\theta(E-E_{\min}-\delta)]\}\\&\equiv j_s'(E)B(E),\end{aligned} \tag{10}$$

where Eq. (10) defines the band-structure enhancement factor $B(E)$. Now all that remains to be done is to obtain a solution to the d-band tunneling probability factor $F(E)$. This is done in Sec. III.

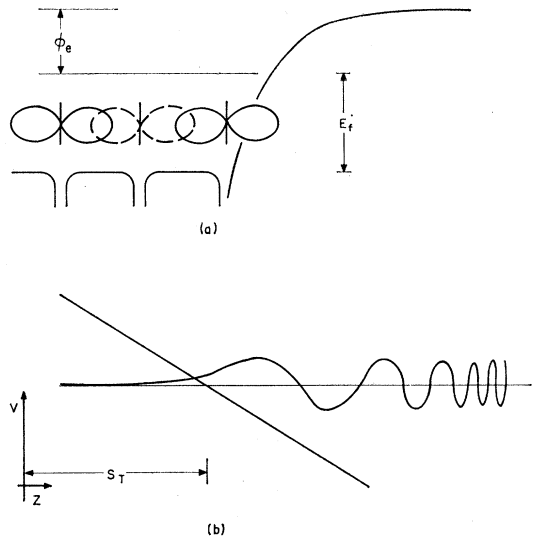

FIG. 2. Schematic diagram of the wave functions for d-band tunneling. (a) The periodic potential with the surface barrier and the tight-binding d orbitals. (b) The final-state electron wave function in the linear field.

III. TUNNELING FROM TIGHT-BINDING BANDS

We have now come to the point where a detailed microscopic analysis of electron tunneling from tight-binding d bands must be provided in order that our study can proceed. Physically the picture is shown in Figs. 2(a) and 2(b). Figure 2(a) is a schematic diagram of the metal potential, unperturbed by the applied field, on which the assumed tight-binding d electrons of Γ_{12} symmetry are also shown. In Fig. 2(b), the free-particle wave function in a constant electric field is shown. In the propagating region, the function is an Airy function while in the classically forbidden region, the solution is of the form $\Psi\sim e^{ik_T\cdot\rho_T}e^{k(z)z}$, where $k(z)=[(2m/\hbar^2)F(s_T-z)]^{1/2}$ and s_T is the classical turning point with respect to some arbitrary origin. The tunneling problem for electrons going between the tight-binding d band and the free state is shown in Fig. 3. Note that for the fields used in field emission, $s_T=(1/F)\times(E_F+\varphi_e-E)$ is usually greater than 20 Å when considering electrons states in the occupied portion of the conduction band in which $E<E_F$, the Fermi energy. The point to be made is that $s_T\gg r_a$, where r_a is some effective d-orbit radius of the order of atomic dimensions. Later we consider overlap integrals of the d orbital with exponential tail of the free-particle wave functions. If we take the $z=0$ point at an atomic center in the last layer of the metal, the d orbital is quite localized within $|z|\lesssim r_a$. Thus, the significant overlap will occur in this region. Since $k(z)=(2mFs_T/\hbar^2)^{1/2}(1-z/s_T)^{1/2}$ and $z/s_T\lesssim 0.1$, we can neglect the z dependence of $k(z)$

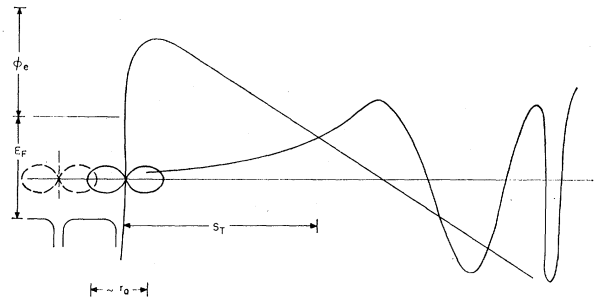

FIG. 3. Schematic diagram of the overlapping wave functions in the presence of the applied field at the surface.

to a first approximation and

$$k(z)\approx[(2m/\hbar^2)(E_F+\varphi_e-E)]^{1/2}.$$

Another technical point to note before proceeding is that the portion of the overlap integral between Ψ and the d orbital, for $\theta>\frac{1}{2}\pi$, that is for $z<0$, is smaller than that part for $\theta<\frac{1}{2}\pi$, for $z>0$, by a factor at least of order e^{-2kr_a} by virtue of the exponential decay of the free-electron tail as it progresses towards more negative z. In the cases of real metal d bands which lie $\sim$5–10 eV below the vacuum potential, $k\sim1$ Å and $r_a\sim2$ Å so the exponential decrease $e^{-2kr_a}\sim0.02$. This feature allows us to make some simplifying mathematical approximations on the d orbits which do not affect the end physical results, namely, that they possess the same inversion or reflection symmetry about the $z=0$ plane in the surface region as they would in the cubic crystal field. Past theories of surface impurities have successfully utilized idealized surface symmetry properties to simplify calculations.[11,12] The present case should be an even better approximation because the errors introduced by this ansatz, which are of order less than unity, are reduced by a factor of order 10^{-2}. The mathematical simplifications which result are well worth it.

According to the accepted theories of tunneling, the phenomenon can be characterized by a tunneling Hamiltonian

$$T_{\mathbf{k},\mathbf{k}'}=\int d^3r\ \Psi_{\mathbf{k}'}^*(\mathbf{r})Tb_{\mathbf{k}}(\mathbf{r}) \qquad (11)$$

with the following physical significance.[13–15] Particles are localized in two distinct regions of space, the "left-hand side" and the "right-hand side," each characterized by some wave function. If the particles in each side are allowed to become aware of the other sides existence, through some coupling Hamiltonian T, then the wave functions of each side will leak into the forbidden intermediate region and overlap. The strength of the coupling and thus transmission function for a particle going from one side to the other is given by the matrix element of Eq. (11). In the case of field emission into vacuum from a metal, the left-hand side wave function $b_{\mathbf{k}}(\mathbf{r})$ is a Bloch function in the metal with an exponentially damped tail in the barrier region. The free-particle function has been discussed. The coupling term T is the surface barrier with the applied field.[16] If the tunneling problem was considered for s-type metal electrons, then the transmission function given by Eq. (11) would be very similar to the usual WKB transmission function.[1–5]

To proceed, it is more expedient to consider linear-combination-of-atomic-orbital-type wave functions for the tight-binding bands. It is assumed that there exists some form of a Wannier-type representation for flat band states in the surface region.[17,18] Then the metal state is written as

$$b_{\mathbf{k}}(\mathbf{r})=(1/\sqrt{N})\sum_{\mathbf{R}_l}e^{i\mathbf{k}\cdot\mathbf{R}_l}a(\mathbf{r}-\mathbf{R}_l), \qquad (12)$$

where the sum is formally over all N lattice sites of the metal. The functions $a(\mathbf{r}-\mathbf{R}_l)=f_{n,2}(r-R_l)Y_{2,m}(\theta,\varphi)$ are atomic-type functions with $l=2$ for d-band states. We will return to this point shortly. Putting Eq. (12) into Eq. (11) yields

$$T_{\mathbf{k},\mathbf{k}'}=(1/\sqrt{N})\sum_{\mathbf{R}_l}e^{i\mathbf{k}\cdot\mathbf{R}_l}H_T(\mathbf{R}_l), \qquad (13)$$

where we have defined

$$H_T(\mathbf{R}_l)=\int d^3r\ \Psi_{\mathbf{k}'}^*(\mathbf{r})Ta(\mathbf{r}-\mathbf{R}_l).$$

In a tight-binding band in which only hopping integrals between nearest neighbors exist, it is also reasonable to expect tunneling to occur only from orbitals centered on atom cores in the surface layer. Furthermore, if the atomic states have $m=0$, then $k_T=0$ in the final state and the phase factor in Eq. (13), accounting for interferences between electrons emitted from various centers will equal unity. Within this picture,

$$T_{\mathbf{k},\mathbf{k}'}=(N_s/\sqrt{N})H_T, \qquad (14)$$

where N_s is the total number of surface atoms and we have called $H_T=H_T(\mathbf{R}_l=0)$. The big problem now is to calculate

$$H_T=\int d^3r\ \Psi_{\mathbf{k}}^*(\mathbf{r})Ta(\mathbf{r}). \qquad (15)$$

In this development, we have assumed that the twofold degenerate Γ_{12} d state will dominate in the tunneling as opposed to the threefold degenerate Γ_{25} states. Under

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[18] D. M. Newns, Phys. Rev. **178**, 1123 (1969).

the assumption that the emitted electron has momentum only in the z direction, this is rigorously true. Furthermore, of the Γ_{12} states, the $\frac{1}{2}[Y_{2,2}+Y_{2,-2}]$ state produces a vanishing matrix element, Eq. (15), under the same assumptions on the final state. Thus the only d state of significance is $Y_{2,0}$. Physically, this is reasonable also since $Y_{2,0}$ has a big lobe extending in the z direction out into the barrier. Thus the d-orbital state has the form $a(\mathbf{r})=f_{n,2}(r)Y_{2,0}(\theta,\varphi)$.

The final state, as discussed earlier, is to a reasonable approximation

$$\Psi_{\mathbf{k}}(\mathbf{r})=c_1e^{-ksr}e^{ikz}$$

with c_1 a normalization constant.

Note that in the simple case of tunneling from a free-electron band, the metal wave function $b_{\mathbf{k}}(\mathbf{r})\rightarrow(1/\Omega^{1/2})\times g(E)e^{-kzz}e^{i\mathbf{k}_T\cdot\mathbf{r}_T}$, where Ω is the crystal volume, and

$$g(E)=(\text{a function of energy of order unity})=\left(\frac{2[\varphi_e+E_F-(\hbar^2/2m)k_z^2]}{(\varphi_e+E_F)}\right)^{1/2}.$$

With the tunneling Hamiltonian $T=-Fz$, the s-band tunneling matrix element from Eq. (11) becomes

$$T_s=(A_s/\Omega^{1/2})s_Tg(E)c_1e^{-kzsT}(-\tfrac{1}{2}Fs_T). \quad (16)$$

This result will be useful later.

The free state can be expressed as a series expansion. It is well known that

$$e^{ikz}=\sum_l[4\pi(2l+1)]^{1/2}i^lj_l(kr)Y_{l,0}(\theta),$$

where j_l is a spherical Bessel function of order l.

Since $j_l(ikr)=e^{(i\pi/2)l}j_l(kr)$,[19] we can write

$$\Psi_{\mathbf{k}}(\mathbf{r})=c_1e^{-ksT}\sum_l[4\pi(2l+1)]^{1/2}e^{i(\pi/2)(l+1)}j_l(kr)Y_{l,0}(\theta).$$

The potential in the barrier region is $T=-Fz=Fr\times\cos\theta$. Also, $\cos\theta=(4\pi/3)^{1/2}Y_{1,0}(\theta)$.

Combining the above thoughts, the tunneling matrix element becomes

$$H_T{}^k=c_1e^{-ksT}\sum_l[4\pi(2l+1)]^{1/2}e^{i(\pi/2)(l+1)}\times[-F(4\pi/3)^{1/2}]\int r^3j_l(kr)f_{n,2}(r)\times\left[\int d\Omega Y_{l,0}(\theta)Y_{1,0}(\theta)Y_{2,0}(\theta)\right]dr. \quad (17)$$

Since

$$\int d\Omega Y_{l,0}Y_{1,0}Y_{2,0}=\frac{\sqrt{15}}{5\sqrt{4\pi}}\left(\frac{3}{\sqrt{7}}\delta_{l,3}-\frac{2}{\sqrt{3}}\delta_{l,1}\right),$$

upon using these results in Eq. (17), performing the sum on l, and doing some manipulation,

$$H_T{}^k=c_1e^{-ksT}\int r^3f_{n,2}(r)[aj_1(kr)+bj_3(kr)]dr, \quad (18)$$

$a=-(\frac{2}{5}\sqrt{15})F$ and $b=(\frac{3}{5}\sqrt{15})F$. Next note that $j_l(kr)=(\pi/2)^{1/2}(1/\sqrt{kr})J_{l+1/2}(kr)$, where $J_{l+1/2}$ is the regular Bessel function of half-integer order. Also we take the radial part of the d orbital to be a Slater function,[20] $f_{n,2}(r)=Cr^{n^*-1}e^{-sr}$, where $s=(Z-s_z)/n^*a_0$, Z is the nuclear charge, s_z is the screening factor, n^* is an effective principle quantum number, C is a normalization constant, and a_0 is the Bohr radius. Typically, s is 1.3–2 Å^{-1}. Equation (18) can thus be written as

$$H_T{}^k=c_1Ce^{-ksT}(\pi/2k)^{1/2}\int_0^\infty e^{-sr}r^{n^*+3/2}\times[aJ_{3/2}(kr)+bJ_{7/2}(kr)]dr. \quad (19)$$

This is just the sum of Laplace transforms of a Bessel function multiplied by its argument raised to some power, of which the standard solutions are given in terms of Gaussian hypergeometric functions.[21] For the sake of completeness, the integrated form of Eq. (19) is presented as

$$H_T{}^k=c_1Ce^{-ksT}\sqrt{\pi}(\tfrac{1}{4}k)(s^2+k^2)^{-(n^*+4)/2}\times\{a[\Gamma(n^*+4)/\Gamma(\tfrac{5}{2})]{}_2F_1[\tfrac{1}{2}(n^*+4),-\tfrac{1}{2}n^*;\tfrac{5}{2};k^2/(s^2+k^2)]+b[\Gamma(n^*+6)/\Gamma(\tfrac{9}{2})](\tfrac{1}{4}k^2)(s^2+k^2)^{-1}\,{}_2F_1[\tfrac{1}{2}(n^*+6),\tfrac{1}{2}(2-n^*);\tfrac{9}{2};k^2/(s^2+k^2)]\}. \quad (20)$$

Since $k^2/(s^2+k^2)$ is always considerably less than unity, we are justified in taking the first two terms in the expansion of ${}_2F_1$,

$${}_2F_1(a,b;c;z)\simeq 1+\frac{\Gamma(a+1)}{\Gamma(a)}\frac{\Gamma(b+1)}{\Gamma(b)}\frac{\Gamma(c)}{\Gamma(c+1)}z=1+\frac{ab}{c}z$$

as an adequate approximation.[22] Then Eq. (20) becomes

$$H_T{}^k\simeq c_1Ce^{-ksT}\sqrt{\pi}(\tfrac{1}{4}k)(s^2+k^2)^{-(n^*+4)/2}\times\left\{a\frac{\Gamma(n^*+4)}{\Gamma(\frac{5}{2})}\left\{1-\frac{k^2}{(s^2+k^2)}[\tfrac{1}{2}(n^*+4)(\tfrac{1}{2}n^*)(\tfrac{2}{5})]\right\}+b\frac{\Gamma(n^*+6)}{\Gamma(\frac{9}{2})}(\tfrac{1}{2}k)^2(s^2+k^2)^{-1}\times\left\{1+\frac{k^2}{(s^2+k^2)}\left[(\tfrac{1}{2}(n^*+6))(\tfrac{1}{2}(2-n^*))\left(\frac{2}{9}\right)\right]\right\}\right\}. \quad (21)$$

Returning to Eq. (16) and comparing with Eq. (21), we can see how the d band transmission function is

[19] *Handbook of Mathematical Functions* (U. S. Government Printing Office, Washington, D. C., 1965), p. 439.

[20] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[21] G. E. Roberts and H. Kaufman, in *Tables of Laplace Transforms* (W. B. Saunders Co., Philadelphia, 1966), p. 60.

[22] Reference 19, p. 566.

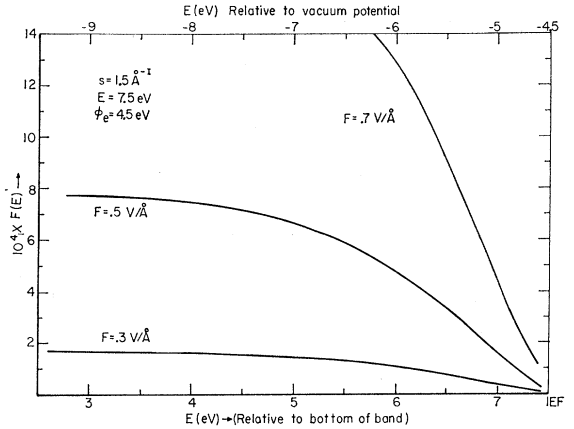

FIG. 4. d-band tunneling probability reduction factor as a function of energy. The applied field is treated parametrically.

given by the s-band tunneling probability multiplied by a slowly varying function. In fact, substituting Eq. (16) into Eq. (21) and Eq. (14) gives

$$T_d{}^k = T_s{}^k\left\{\left(\frac{N_s}{A_s}\right)\left(\frac{\Omega}{N}\right)^{1/2} \times \frac{C\sqrt{\pi}2}{s_T g(E)(E_F+\varphi_e-E)}\tfrac{1}{4}k(s^2+k^2)^{-(n^*+4)/2} \times\left\{a\frac{\Gamma(n^*+4)}{\Gamma(\frac{5}{2})}\left[1-\frac{k^2}{(s^2+k^2)}(\tfrac{1}{10}(n^*+4)n^*)\right] +b\frac{\Gamma(n^*+6)}{\Gamma(\frac{9}{2})}(\tfrac{1}{2}k)^2(s^2+k^2)^{-1} \times\left[1+\frac{k^2}{(s^2+k^2)}\left(\frac{(n^*+6)(2-n^*)}{18}\right)\right]\right\}\right\}. \quad (22)$$

The big term in brackets multiplying T_s is just the square root of the slowly varying function $F(E)$ referred to in Eqs. (9) and (10). Note that we have now called $T_{\mathbf{k},\mathbf{k}'}=T_d{}^k$ in order to distinguish between s- and d-band tunneling. To go farther, we must specify an effective principle quantum number n^*. In this first study, we simply take $n^*=2$ as this choice has most of the qualitative features of a more complicated system. With this choice, there is an outer orbital, node at some finite radius, and an inner core shell. The atomic normalization in this case is $C=s^{5/2}/(3\pi)^{1/2}$. Using the appropriate values for a and b we thus get from Eq. (22)

$$F(E)=(T_d/T_s)^2=(N_s/A_s)^2(\Omega/N) \times[s_T g(E)(E_F+\varphi_e-E)]^{-2}\left(\frac{F^2k^2}{20}\frac{s^5}{(s^2+k^2)^6}\right) \times\left(\frac{542k^2}{(s^2+k^2)}-180\right)^2. \quad (23)$$

This is the important end result of this section, the ratio of d-band to s-band tunneling probabilities at a given energy, which will allow us to determine the band-structure enhancement factor $B(E)$ in Eq. (10) and thus permit us to understand the TED of field emitted electrons from our model noble metal. The numerical implications appear in Sec. IV.

IV. RESULTS, DISCUSSION, AND CONCLUSIONS

The first object of interest is the numerology related to the slowly varying part of the d-band tunneling probability, the preexponential factor $F(E)$. Recall that $D_d(W)=F(W)|_{W=E}D_s(W)$, where $D_s(W)\sim e^{W/d}$ in the equation for the TED. Equation (23) gives the d-band preexponential in terms of the parameters of the system. The factor N/Ω is the atomic density in the metal which we take to be 10^{23} atoms/cm^3. N_s/A_s is the density of atoms on the surface plane taken to be 2×10^{15} atoms/cm^2. The relationship between the classical turning point s_T and the wave number k to other parameters has already been stated. We take $\varphi_e=4.5$ eV and $E_F=7.5$ eV. The parameter s in the Slater function $=Z/n^*a_0 \simeq n^*/r$, where r is approximately some sort of shell radius.[23] For tight binding d-band orbitals, this radius should be less than half the lattice constant. With $n^*=2$, as we have assumed, $s>1.3$ Å^{-1}.

With the above-mentioned choice of parameters, the preexponential tunneling factor $F(E)$ is drawn as a function of energy for several different values of electric field used in field-emission experiments with $s=1.5$ Å^{-1} in Fig. 4. In Fig. 5, s is treated parametrically with a constant field $F=0.5$ V/Å. The slope of the linear FN line is also shown for comparison. As expected, in all cases the value of $F(E)$ is much smaller than unity reflecting the fact that tight-binding electrons are not only tightly bound with respect to conduction processes but also with respect to tunneling. Although numerical significance should not be given to these results to better than an order-of-magnitude estimate, the relative trends as parameters are varied is physical within the marked limits. The field strength used in experiments falls mostly between 0.3 and 0.5 eV/Å. Figure 4 shows that there is nothing wrong with the qualitative ideas presented here in this range of fields; that is, $F(E)$ is well behaved and relatively slowly varying with energy below the Fermi surface compared to the exponential s-band result. Of greater interest are the results shown in Fig. 5. Here it is seen that the tunneling probability at a given energy is extremely sensitive to the choice of s, but once s is chosen $F(E)$ varies slowly with E for 1 Å$^{-1}<s<1.5$ Å^{-1}. Upon reflection, this is also quite expected. The parameter s is a measure of how tightly bound the d electron is with smaller s implying less tightly-bound electrons

[23] K. S. Pitzer, *Quantum Chemistry* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1953), p. 82.

which should be much more free to tunnel. In fact, at a given energy we would roughly expect the $F(E)$ factor to vary as an inverse exponential of s as it indeed seems to do. From previous arguments, we would expect the value of s for truly tight-binding bands to be somewhere in the range $1.3\ \text{Å}^{-1} \lesssim s \lesssim 1.5\ \text{Å}^{-1}$. As can be seen in Fig. 5, within this small span of s, $F(E)$ varies by a factor of 10, falling in the range $2\times10^{-4} \lesssim F(E) \lesssim 2\times10^{-3}$. [See note added in proof.] Consequently, our estimates of d-band tunneling current will be uncertain by this amount. In any event, we can see that the tunneling probability for a given d electron will be roughly 10^{-3} times that of an s electron at the same energy. The total d-electron tunneling current will be increased by the density-of-states type factor, but not in the dramatic manner in which we had hoped, as a result of the small tunneling probability. We should also note that the wide basically d bands in transition metals such as tungsten are not so tightly bound and thus the s parameter would tend to be a bit smaller than in the model noble metal.[24] Consequently, the appropriate value for $F(E)$ could be greater than 10^{-2} and it might then be possible to unambiguously observe certain band-structure effects. However, the tight-binding approximation breaks down in this case and another

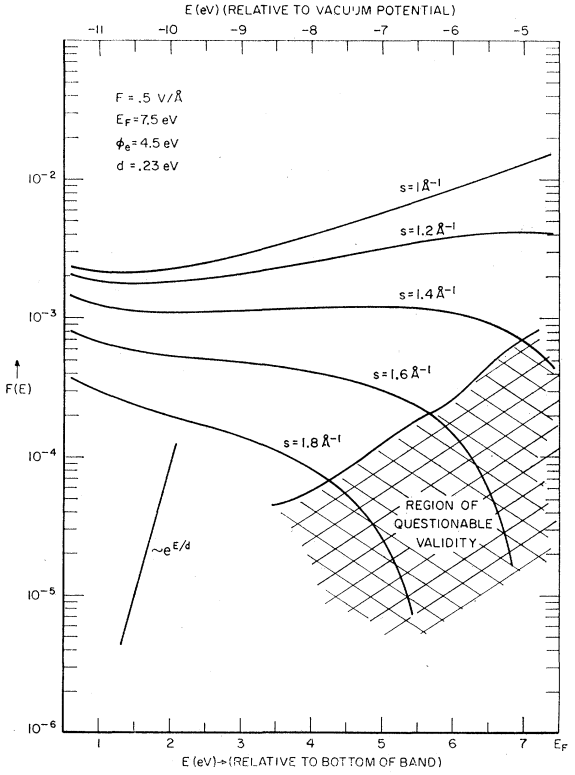

FIG. 5. d-band tunneling probability reduction factor as a function of energy. The tight-binding parameter s is treated parametrically. Also shown is the slope of the s-band tunneling probability. The region of questionable validity is cross-hatched.

[24] L. F. Mattheiss, Phys. Rev. **139**, 236 (1965.)

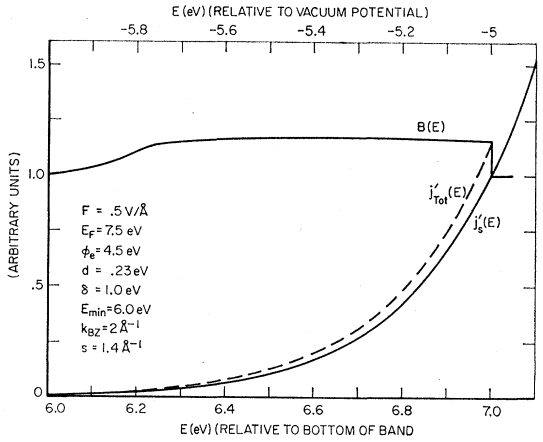

FIG. 6. Band-structure enhancement factor $B(E)$ and the TED as a function of E for $\delta = 1.0$ eV.

method must be devised. We return to this point when we discuss the "anomalous" tungsten data obtained by Swanson and Crouser.[8]

Next we consider the band-structure enhancement factor $B(E)$ given by Eq. (10). It is here that the enhancement from the density-of-states effects is weighed relative to the decreasing factor of the d-band tunneling probability. To get a quantitative feel for the problem some tenable parameters must be assigned to the band structure. Consider the model metal band to be such that the band width $\delta = 1$ eV and let $E_{\min} = 6$ eV, so that the top of the d band lies 0.5 eV below the Fermi level. Also consider the case when $E_{\min} = 6.75$ eV and $\delta = 0.25$ eV. The distance in k space from Γ to the zone face, k_{Bz}, is of the order of $2\pi/a$ with a the lattice constant. As an estimate, we take $k_{Bz} = 2\ \text{Å}^{-1}$. Other values used are $s = 1.4\ \text{Å}^{-1}$, $F = 0.5$ V/Å, and $d = 0.23$ eV. Since we are really considering a twofold degenerate Γ_{12} band, which we assume is not split by the crystal field away from Γ, the degeneracy parameter n is set equal to two. Spin degeneracies have already been included in J_0.

From Eqs. (10) and (23), $B(E)$ is drawn as a function of E for the chosen parameters in Figs. 6 and 7. The sharp cutoff at $E = E_{\min} + \delta$ is an artifact of the model and in reality would be rounded. Also shown in Figs. 6 and 7 are the predicted shapes of the TED. It is seen that the hump in the TED, for the very narrow band, a manifestation of density-of-states and band-structure effects, could certainly be detected experimentally although in not as obvious a manner as might be expected from looking at a density-of-states curve. This band-structure effect has arisen from density-of-states effects and not Fermi-surface effects discussed by others.[4,5,8] Certainly the final treatment will have to include both contributions. However the purpose here has been to demonstrate that density of states and nonparabolic bands give effects that are just as, if not more, important in determining the TED than Fermiology considerations.

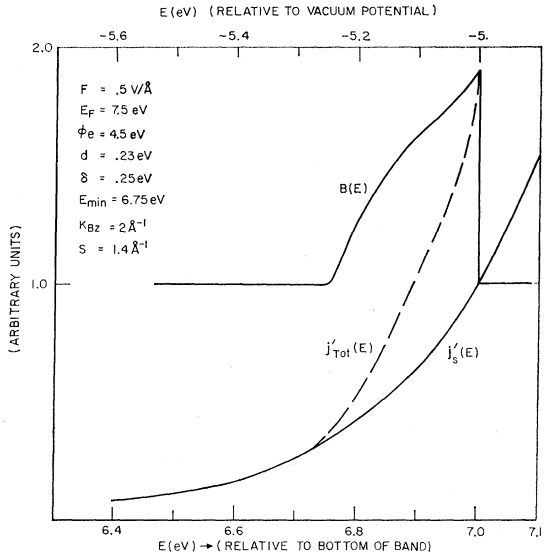

FIG. 7. Band-structure enhancement factor $B(E)$ and the TED as a function of E for $\delta=0.25$ eV.

In actual practice, the best way to get information from observed TED is to divide this by the s-band tunneling probability thus giving the band-structure enhancement factor $B(E)$. Any structure in $B(E)$ can then be interpreted within a band-structure framework. There are many technical problems though in this procedure. With the present integral energy analyzers commonly used in experiments it is only possible to measure a TED down to $\sim$0.5 eV below the Fermi energy. In this region the FN expression for an s-band TED is reasonably valid. However with the eventual adaption of differential energy analyzers, it will be possible to accurately measure a TED to several volts below the Fermi energy. As Plummer has pointed out, when one looks below 0.5 eV from the Fermi energy, the asymptotic expansions used in the derivation of the FN tunneling break down dramatically.[25] It will be very important to retain higher-order terms in the s-band tunneling probability so that a meaningful separation between $j_s'(E)$ and $B(E)$ can be effected in the total energy distribution $j_{tot}'(E)=j_s'(E)B(E)$. Thus one must have an accurate theoretical estimate of $j_s'(E)$ in order to infer values of $B(E)$ from measured values of $j_{tot}'(E)$.

Unfortunately it is not a very straightforward procedure to go from values of $B(E)$ to a unique statement about the d-band structure. Probably the only thing that will be able to be said about the band structure from measured values of $B(E)$ is that in the energy region in which $B(E)$ displays some hump, there is a reasonably flat nonparabolic band. It will be hard to obtain quantitative information from either the magnitude or the energy dependence of the hump in $B(E)$. In the final analysis, it appears possible that we will be able to see some sort of band-structure effects in the TED but it will not be very easy to obtain much quantitative information from the observed effects, at least as far as band-structure information is concerned. This situation results from a number of factors. The first is related to the relative uncertainty in an accurate description of d-band tunneling. The extreme sensitivity of $F(E)$ on our choice of s illustrates this problem. The second problem arises from the fact that either we must be able to unfold $B(E)$ so as to separate the energy-dependent tunneling probability from the energy-dependent two-dimensional density-of-states factor. Alternatively, we can fold together an assumed band-structure factor with an assumed tunneling probability and adjust parameters until the measured and predicted values of $B(E)$ coincide. Both procedures suffer from the same deficiencies. We must have a pretty good idea as to what the answer is before we start. Actually, this is not so bad though since most other band-structure and Fermi-surface experiments such as photoemission, optical studies, and de Haas–Van Alphen effects require much the same conditions. Second, even if we are able to reproduce the $B(E)$ factor with a particular choice of tunneling probabilities and density of states, there is little guarantee that we have hit on a unique solution to the problem.

Next we should make some comment with regards to the "band-structure hump" in the TED of electrons emitted from the (100) face of tungsten observed by Swanson and Crouser.[8] They observe a hump in the TED, qualitatively similar to the hump in the theoretical TED shown in Fig. 7, from about 0.2–0.5 eV below the Fermi energy for electrons emitted in the (100) direction or along ΓH in the Brillouin zone. In the calculated band structure of W, Mattheiss and Watson[26] have considered various spin-orbit splitting parameters ξ_{5d}, where the Γ_{12} band of symmetry Δ_7 crosses the Δ_7 band of Γ_{25}, at a position roughly 0.4 eV below the calculated Fermi energy. The splitting causes a band gap whose magnitude depends upon the strength of ξ_{5d}. Also the position of the Fermi energy relative to the band gap depends upon ξ_{5d}. Swanson and Crouser argue that the influence of the gap on the topology of constant energy surfaces whose energies fall within the gap may be related to the TED through Stratton's Fermi-surface integral. They then suggest that the presence of the hump or excess emission current is related to the splitting, the subsequent energy gap, and the resulting Fermi-surface shapes. On the most naive level, one might expect that the presence of an energy gap would suggest a decrease in current for energies within the gap due to the absence of allowed states. Thus, the TED would show a depression rather than a hump.

In light of the Swanson and Crouser interpretation, an alternative point of view which follows from the

[25] E. W. Plummer (private communication).

[26] L. F. Mattheiss and R. E. Watson, Phys. Rev. Letters **13**, 196 (1964).

ideas put forth in this paper is offered. In Fig. 8, the relativistic energy bands along ΓH, calculated by Loucks, are shown.[27] Note that the originally unhybridized Δ_7 band emanating from Δ_7^+ is quite flat for $k \lesssim 0.3\ k_{Bz}$ at an energy about 0.4 eV below the Fermi energy. For the cubic crystal ΓH is both normal and transverse to the emission direction for certain values of the angle φ. The tunneling from this portion of the d band could be qualitatively very similar to the type of tunneling described in this paper. The electrons might be somewhat tightly bound but the flat band gives a bigger transverse density-of-states-type factor. Extremal points in this band occur at about 0.3 and 0.5 eV below the Fermi surface resulting in $\partial E/\partial k_T$ going to zero and thus another large density-of-states type factor. Consequently, in the range $0.3 \lesssim E \lesssim 0.5$ eV below the Fermi energy, the range in which the hump in the TED is observed, there are large band-curvature or density-of-states-type factors moderated by a smaller tunneling probability. The observed behavior has just the characteristics that would be expected from a material with the band structure calculated by Loucks, when interpreted in terms of the present analysis. Although these ideas are quite speculative, their intuitive appeal seems to warrant presentation as another way of looking at the Swanson and Crouser data.

In summary, we have reformulated the theory of field emission to allow for some new band-structure-type effects not present in parabolic energy bands. The theory has shown that in some senses, density-of-states-type information is obtainable from the TED of field-induced tunneling electrons. The small amount of experimental data which possibly contains such band-structure information is quite consistent with the ideas put forth here, although it is not claimed to be positive proof of the theory.

There are, however, a number of weaknesses in the theory which might be dealt with in future work. Although it is not felt that these points invalidate any of the qualitative conclusions given here, quantitativeness may suffer. An enumeration of some of these points is as follows. First, it might be more desirable to include tunneling matrix elements from electrons centered on lattice sites other than surface atoms As Wood points out, at least for the case of d electrons in iron, it is not at all obvious that linear-combination-of-atomic-orbital-type wave functions are a good approximation for all d states.[28] Some of the d states have wave functions nearly as extensive as the s-band states. However, the question of the nature of d electrons in transition metals is still an open question with regards to energy-band calculations and magnetism theory. Until this question is answered, it will be quite difficult to get a truly accurate picture of tunneling from d bands.

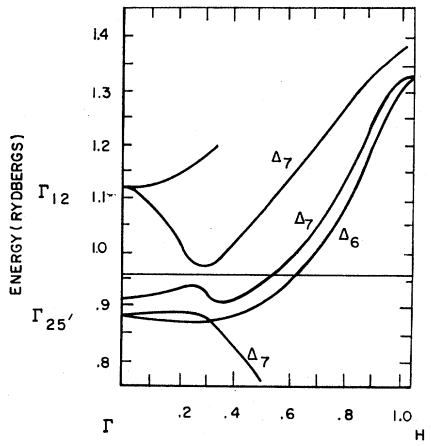

FIG. 8. Portion of the tungsten band structure along ΓH and near the Fermi energy.

Another difficult point is concerned with the form of tunneling matrix elements. There exist several problems in doing tunneling theory as a result of the fact that tunneling, as usually formulated, is not a mathematically well-posed problem.[15] We have used the Oppenheimer formulation of tunneling matrix elements, originally intended for treating field ionization of isolated atoms.[16] Although this is not a rigorously correct from the mathematical point of view due to the over completeness of the sets of states used, more accurate calculations of the field ionization of isolated atoms[29,30] and atoms in the presence of a surface[31] have shown that the Oppenhemier or rearrangement collision[32] point of view seems to provide reasonable results. Fundamentally, field emission from metals is very similar to field ionization of isolated atoms, the major distinction arising only from the choice of initial states, whether they are Bloch functions or atomic functions. Since the Oppenheimer theory is reasonable for atoms, we assume that it is an adequate first approximation for atomiclike d states in metals. Furthermore, since we are only calculating the ratio of d- to s-band tunneling within the Oppenheimer approximation, we might imagine the errors to be even smaller.

Still another problem is related to the difficulty in doing three-dimensional tunneling problems. In most cases, some sort of artificial decoupling must be assumed to transform the wave functions into a product form $\Psi(\mathbf{r}) \sim \Psi_1(\varrho_T)\Psi_2(z)$ as was discussed by Bennett and Duke.[33] The present work has not been able to come to full grips with this problem. In order for calculations to proceed, we had to assume a band structure in which energy was a function of the magnitude of k but not of the direction. This assumption is equivalent to a one-

[27] T. L. Loucks, Phys. Rev. Letters **14**, 212 (1965).
[28] J. H. Wood, Phys. Rev. **117**, 714 (1960).
[29] C. Lanczos, Z. Physik **68**, 204 (1931).
[30] M. H. Rice and R. H. Good, J. Opt. Soc. Am. **52**, 239 (1962).
[31] D. S. Boudreaux and P. H. Cutler, Phys. Rev. **149**, 170 (1966).
[32] T. Y. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962), p. 211.
[33] A. J. Bennett and C. B. Duke, Phys. Rev. **162**, 578 (1967).

dimensional tunneling assumption although it is not as blatantly apparent. We were able, however, to avoid the parabolic band restriction and in this sense some interesting band-structure effects could enter.

Lastly, when all is said and done we really considered only tunneling from d-band states of Γ_{12} in which $m=0$ and thus $k_T=0$, at least in evaluating transmission functions. One of the advantages of the Oppenheimer formulation is that three-dimensional tunneling matrix elements can be handled. Although by considering the easier $m=0$ state, we in effect did not treat all the ramifications of transverse momentum, this is only a technical point which can be straightened out by a more exhaustive calculation within the framework of the theory presented here.

In spite of the limitations just cited, it is felt that the basic physics illustrated by this model calculation is sound. All the qualitative and even semiquantitative conclusions should stand up under the test of a more accurate calculation or experimental data. We have seen that band-structure and density-of-states information is present in the TED of field-emitted electrons. Due to the assumed tight-binding character of the d electrons, a reduced tunneling probability lowers the magnitude of the density-of-states peaks in the TED such that the structure is not as pronounced as it would be if the d-band tunneling probability was the same as the s-band probability. However this work, with its inherent weaknesses, should serve as a useful guide in future theoretical work and may provide some useful insight into the interpretation of new experimental data.

Note added in proof. Due to an inconsistency in the normalization of the d electron wave function, the ratio of the d to s electron tunneling probability, $F(E)$, given by Eq. (23) should be multiplied by 4π. It is then noted that the d-band tunneling probability is about 10^{-2} times the s-band probability. These results are in good agreement with the ion-neutralization experiments of Hagstrum in which he noted that d-band tunneling to the incident ion is suppressed by a factor of order 10^{-1}–10^{-2} compared to s-band tunneling at the same energy,[34,35] for reasons similar to those noted in the present paper.

ACKNOWLEDGMENTS

Many fruitful discussions with Dr. E. W. Plummer and Dr. R. D. Young on band-structure effects in field emission are appreciated.

[34] H. D. Hagstrum, Phys. Rev. **150**, 495 (1966); H. D. Hagstrum and G. E. Becker, *ibid.* **159**, 572 (1967).

[35] W. E. Spicer, in *Optical Properties and Electronic Structure of Metals and Alloys* edited by F. Abeles (North-Holland Publishing Co., Amsterdam, 1966), p. 312.