Table II. The change of the principal energy gaps in eV for a change in form factor of +0.01 Ry.

	V_{111}	V_{220}	V_{311}	V_{222}
$\Gamma_{25'}-\Gamma_{15}$	−0.116	−0.052	0.222	−0.265
$\Gamma_{25'}-\Gamma_{12'}$	−0.132	−0.162	−0.190	−0.154
X_4-X_1	−0.094	0.018	0.176	−0.102
$\Gamma_{25'}-X_1$	−0.154	−0.012	0.274	−0.206
$L_{3'}-L_1$	−0.018	0.192	0.258	−0.152

given in Table II.

The simplicity of the $(1s)^2$ cores of carbon have inspired orthogonalized plane-wave[17] band calculations, but it was not obvious a priori that the EPM method would be successful for diamond. The success of this method presumably relies on the applicability of the Phillips cancellation theorem.[18] However, the absence of p core states means that the kinetic energy of the valence p electrons is not cancelled.[19] The apparent success of the EPM method for diamond probably arises from the fact that the valence p states have small probability of being in the core because of the form of the p wave function, and therefore complete cancellation is not imperative for these states.

One of us (MLC) benefitted from conversations with Dr. Frank Herman and Professor J. C. Phillips.

*Work supported by the National Science Foundation.
†National Science Foundation Predoctoral Fellow.
‡Alfred P. Sloan Fellow.

[1]W. C. Walker and J. Osantowski, Phys. Rev. 134, A153 (1964).
[2]H. R. Philipp and E. A. Taft, Phys. Rev. 136, A1445 (1964); 127, 159 (1962).
[3]J. C. Phillips, Phys. Rev. 139, A1291 (1965).
[4]D. M. Roessler, thesis, University of London, 1966 (unpublished).
[5]M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).
[6]J. C. Phillips, Phys. Rev. 112, 685 (1958); D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters 9, 94 (1962); D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters 9, 389 (1962); D. Brust, Phys. Rev. 134, A1337 (1964).
[7]T. K. Bergstresser, M. L. Cohen, and E. W. Williams, Phys. Rev. Letters 15, 662 (1965).
[8]M. L. Cohen and J. C. Phillips, Phys. Rev. 139, A912 (1965).
[9]L. Kleinman and J. C. Phillips, Phys. Rev. 125, 819 (1962).
[10]K. H. Bennemann, Phys. Rev. 133, A1045 (1964).
[11]M. Renninger, Z. Krist. 97, 107 (1937).
[12]M. Renninger, Acta Cryst. 8, 606 (1955).
[13]R. W. G. Wyckoff, Crystal Structures (Interscience Publishers, New York, 1963).
[14]E. O. Kane, to be published.
[15]C. D. Clark, P. J. Dean, and P. V. Harris, Proc. Roy. Soc. (London) A277, 312 (1964); C. D. Clark, J. Phys. Chem. Solids 8, 481 (1959).
[16]P. J. Dean, E. C. Lightowlers, and D. R. Wright, Phys. Rev. 140, A352 (1965).
[17]F. Herman, Phys. Rev. 93, 1214 (1954); Proceedings of the International Conference on the Physics of Semiconductors, Paris (Dunod, Paris, 1964), p. 3.
[18]P. W. Anderson, Concepts in Solids (W. A. Benjamin, Inc., New York, 1963), p. 66.
[19]L. Kleinman and J. C. Phillips, Phys. Rev. 116, 880 (1959).

RICHARDSON-SCHOTTKY EFFECT IN INSULATORS*

P. R. Emtage and J. J. O'Dwyer†
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania
(Received 31 January 1966)

The Richardson-Schottky formula for thermionic emission from a metallic cathode into the conduction band of an insulator is frequently[1] stated as

$$J_S = \frac{4\pi e m (kT)^2}{h^3} e^{-(\varphi_0 - \Delta\varphi)/kT}. \quad (1)$$

In this expression φ_0 is the work function, and the Schottky term is given by

$$\Delta\varphi = (e^3 F_c/\epsilon)^{1/2}, \quad (2)$$

where ϵ is the dielectric constant, and F_C the field strength immediately in front of the cathode. It has recently been pointed out by Simmons[2] that this expression is invalid when the mobility of the electrons in the dielectric is low, for if one determines the density of current carriers in the insulator, n, from the relationship

$$J = ne\mu F, \quad (3)$$

one may then find that n becomes so large that back-diffusion from the dielectric to the metal will occur. Unfortunately Simmons's discus-

sion omits mention of the relative importance of space-charge effects and of diffusion currents, and of the cases in which we should expect one effect or the other to dominate.

The model under consideration is an insulator free of trapping centers, uncharged, and containing no conduction electrons in its normal state; the only space-charge effects that occur are associated with injected conduction electrons. We propose to show that, under these circumstances, it is usually possible to consider effects that occur near the cathode separately from effects that occur in the bulk of the dielectric.

(a) Bulk effects.—For the moment we suppose that the emission characteristics of the cathode-dielectric system are known, the current density being written

$$J = J(F_c, \varphi_0), \tag{4}$$

where φ_0 is the metal dielectric work function. The standard treatment of space-charge limited emission[3,4] is to suppose that diffusion currents are negligible, and to use Poisson's equation

$$\partial F/\partial x = 4\pi ne/\epsilon, \tag{5}$$

which, together with (3), yields

$$F = \{F_c^2 + 8\pi Jx/\epsilon\mu\}^{1/2}. \tag{6}$$

A characteristic length L defining the rate of change of carrier density and electric field may be found,

$$L = n\Big/\frac{\partial n}{\partial x} = \epsilon F_c/4\pi ne. \tag{7}$$

From Eq. (6) we see that the condition that space-charge effects shall be negligible is

$$8\pi Jd/\epsilon\mu \ll F_c^2, \text{ or } F_c \gg 8\pi ned/\epsilon. \tag{8}$$

These results hold only if the diffusion current, $J_{\text{diff}} = kT\mu\partial n/\partial x$, is much less than the field current. The ratio of these currents is readily found to be

$$\begin{aligned} J_{\text{diff}}/J &= 4\pi kTn_0/\epsilon F_c^2 \\ &= \tfrac{1}{3}(\text{carrier thermal energy density})/ \\ &\quad (\text{electrostatic field energy density}). \end{aligned} \tag{9}$$

(b) The cathode current.—In the neighborhood of the cathode an electron has a potential energy

$$e\varphi = e\varphi_0 - eF_c x - e^2/4\epsilon x, \tag{10}$$

the term $e^2/4\epsilon x$ being due to image forces. This function is sketched in Fig. 1. The potential reaches a maximum value $\varphi_0 - \Delta\varphi$ at a distance x_0 from the interface, where $\Delta\varphi$ is given by Eq. (2) and where

$$x_0 = (e/4F_c\epsilon)^{1/2}. \tag{11}$$

It is now of interest to consider some typical figures. Suppose that

$$F_c = 10^5 \text{ V/cm}, \quad \epsilon = 6, \quad n = 10^{16}/\text{cm}^3, \quad T = 300^\circ\text{K};$$

one finds, from Eqs. (9), (8), and (7),

$$J_{\text{diff}}/J = 0.01,$$

space charge small if $d < 1500$ Å,

$$L = 3000 \text{ Å},$$

while from Eqs. (2) and (11) we obtain

$$\Delta\varphi = 0.05 \text{ eV}, \quad x_0 = 25 \text{ Å}.$$

The value of n chosen here is very large, corresponding to a work function of only 0.2 eV, and Schottky emission is not normally observed for fields less than 10^5 V/cm. We may therefore feel confident that the ratio J_{diff}/J will be small, provided that the metal-insulator contact is a non-Ohmic contact, and that the characteristic length associated with the variation of the space charge will be at least several thousands of angstrom units. However, since the rapid variations in the potential (10) take place within 50 Å in front of the cathode, the field F_c in (10) may be regarded as being nearly constant, and space-charge effects can be ignored altogether in the calculation of the

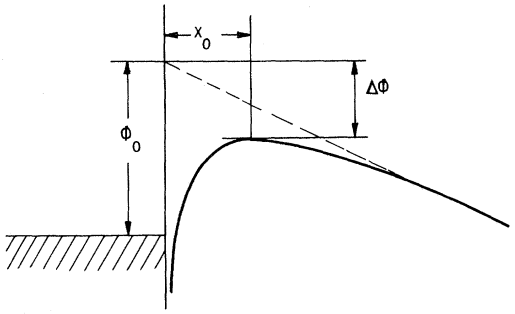

FIG. 1. Potential energy of an electron near the cathode surface.

cathode characteristics.

When the mobility is low, diffusion currents control the total cathode current; we therefore write

$$J = ne\mu\partial\varphi/\partial x + kT\mu\partial n/\partial x, \tag{12}$$

with φ the potential given by (10). On taking J and μ to be constant, and solving for n, we obtain

$$n(x) = e^{-e\varphi/kT}\left\{N + \frac{J}{kT\mu}\int_0^x e^{e\varphi/kT}dx'\right\}, \tag{13}$$

with the boundary condition

$$N = 2(2\pi mkT/h^2)^{3/2}, \tag{14}$$

being the density of electrons at $x = 0$. To calculate the integral in (13) with the potential (10) we require the following results:

$$\int_0^\infty e^{-(ax + b/x)}dx = (b/a)^{1/2}\int_2^\infty \frac{y}{(y^2-4)^{1/2}}\exp[-(ab)^{1/2}y]\,dy$$

$$\simeq 1/a \text{ if } (ab)^{1/2} \ll 1, \tag{15}$$

$$\simeq \pi^{1/2}(b/a^3)^{1/4}\exp[-2(ab)^{1/2}] \text{ if } (ab)^{1/2} \gg 1. \tag{16}$$

$$\int_0^x e^{-(ax + b/x)}dx \simeq \int_0^\infty e^{-(ax + b/x)}dx - \frac{1}{a}e^{-ax} \text{ if } x \gg (b/a)^{1/2}. \tag{17}$$

Using (15) and (17) in (13) we obtain the low-field approximation

$$n(x) = J/e\mu F + \exp(eFx/kT) \times\{N\exp(-e\varphi_0/kT) - J/e\mu F\}.$$

To avoid divergences the coefficient of the exponential term must vanish and

$$J = N\exp(-e\varphi_0/kT)e\mu F, \tag{18}$$

which is the usual result for low fields.

For the high-field case we use (16) and (17) in (13) to obtain, for large values of x,

$$n(x) = J/e\mu F + \exp(eFx/kT)\left\{N\exp(-e\varphi_0/kT) + \frac{J}{kT\mu}\frac{(\pi kT)^{1/2}}{(4eF^3\epsilon)^{1/4}}\exp(-\Delta\varphi/kT)\right\},$$

from which

$$J = N\mu\left(\frac{kT}{\pi}\right)^{1/2}(4eF^3\epsilon)^{1/4}\exp[-e(\varphi_0 - \Delta\varphi)/kT], \tag{19}$$

and

$$n = J/e\mu F.$$

Equation (19) gives the current for the extreme case in which the current in the insulator is diffusion controlled, while the Schottky current, Eq. (1), represents the greatest current that can flow across the interface when no scattering occurs in the insulator. The ratio of these two currents is

$$J_S/J = e/2\mu m^{1/2}(eF_c{}^3\epsilon)^{1/4}. \tag{20}$$

The cathode current is diffusion controlled when this ratio is greater than unity, and Eq. (19) should then be used; when the ratio is less than unity the Richardson-Schottky equation will hold. The ratio may be set in a more perspicuous, though less useful, form by expressing the mobility in terms of the electron mean free path, λ, and velocity, v,

$$\mu = e\lambda/mv.$$

One then finds, from Eqs. (2), (11), and (20)

$$J_S/J = (mv^2/\Delta\varphi)^{1/2}x_0/\lambda.$$

The appropriate value of v in this expression is doubtful, but clearly the ratio of energies is of the order of unity. We therefore reach the intuitively obvious result that diffusion effects become important when the mean free path of the electrons is comparable with the distance from the cathode to the potential maximum.

In practical units, Eq. (20) shows that diffusion limiting becomes important when the inequality

$$\mu F^{3/4} \lesssim 5 \tag{21}$$

is satisfied, μ being in units of cm^2 V/sec, and F in MV/cm.

We have not been able to find any unambiguous evidence of the existence of diffusion-limited Schottky emission in the literature.

---

*This research was supported by the Advanced Research Projects Agency, Director for Materials Sciences and was technically monitored by the Air Force Office of Scientific Research under Contract No. AF 49(638)-1245.

†Present address: University of New South Wales, Kensington, Australia.

[1]H. K. Henisch, Metal Rectifiers, (Oxford University Press, New York, 1949), p. 98.

[2]J. G. Simmons, Phys. Rev. Letters 15, 967 (1965).

[3]Z. Croitoru, Progr. Dielectrics 6, 103 (1965).

[4]M. Lampert, Rept. Progr. Phys. 27, 329 (1964).