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Thomas-Fermi Approach to Impure Semiconductor Band Structure

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The density of states in highly impure semiconductors is studied using a semiclassical or Thomas-Fermi type approximation. The "local" density of states is assumed proportional to $(E-\mathcal{V})^{1/2}$, where $\mathcal{V}$ is the local potential. The problem then reduces to the calculation of the distribution function for the potential, which is found to be a Gaussian in the high-density limit. It is clear that this approach predicts tails on *both* band edges which are identical except for a multiplying factor of $(m^*)^{3/2}$, the density-of-states mass. The important contributions to the potential variation near the average potential are shown to arise from fluctuations in impurity clusters whose volume is of the order of the cube of the screening length. For energies far below the average potential the important cluster sizes are much smaller than the screening length cubed. Their size is determined by the kinetic energy of localization, an effect which is not accounted for by the $(E-\mathcal{V})^{1/2}$ assumption. The Thomas-Fermi method involves a number of approximations, all of which are valid in the limit of high density. The most serious approximation results from the improper treatment of the kinetic energy of localization which requires $(na_0^{*3})^{1/12}\gg 1$ for validity. Because of this requirement, the method is never highly accurate in any attainable concentration range. The effect of potential fluctuations on tunnel diode *I-V* characteristics is also studied. The results agree satisfactorily with experimental studies of silicon junctions by Logan *et al.*

I. INTRODUCTION AND CONCLUSIONS

THE problem of the band structure of impure semiconductors has been most extensively studied in one dimension.[1] Quantitative three-dimensional calculations have been performed by Parmenter[2] using perturbation theory and assuming a screened Coulomb model for the impurities. More recently Wolff[3] has used a more rigorous perturbation-type approach. He treats electron-electron effects *ab initio* and justifies the screened Coulomb model for the impurities in the high-concentration limit. In this limit electron-electron effects introduce a relatively small change in effective mass from the pure crystal value. Electron-electron correlation also introduces an additive energy constant, not correctly given by taking the screened Coulomb model literally. A treatment similar to Wolff's has also been given independently by Bonch-Bruevich.[4]

More recent work by Bonch-Bruevich[5] and Keldysh[6] has been presented at the Exeter Conference. Bonch-Bruevich makes a semiclassical or Thomas-Fermi type of approximation so that his approach has a good deal of overlap with the present paper. An outline of our approach was also given at Exeter.[7] A different approach using spectral moments calculated by perturbation theory was also outlined by the author at Exeter[7] and will be treated more fully in a forthcoming publication.

In the present paper we make the screened Coulomb approximation at the outset. We further make a semiclassical or Thomas-Fermi type approximation wherein we assume that the local potential is sufficiently slowly varying that a local density of states can be defined just as if the potential were constant. The calculation of the over-all density of states then reduces to the calculation of the distribution function for the potential. We find that with suitable further approximations the distribution function for the potential has a Gaussian form. Keldysh[6] also finds a Gaussian dependence similar to ours but with different numerical factors for the half-width.

In Sec. II we describe our model Hamiltonian. In Sec. III we make the "uniform cluster" approximation. The probability of finding m atoms in a sphere of volume w is computed rigorously but the potential is approximated by taking the uniform average over the sphere. We show that the most important fluctuations occur for a sphere size

$$w_D \sim 4\pi\kappa_D^{-3}/3,$$

where κ_D is the reciprocal screening length. Fluctuations of m with w fixed lead to a Gaussian distribution for the potential. The kinetic energy of localization is also treated on this model. For energies very far below the average potential, cluster sizes $w\ll w_D$ become important. The kinetic energy of localization is essential in determining the optimum value of w.

In Sec. III we treat the Thomas-Fermi approximation less crudely than in Sec. II. The potential distribution function is rigorously represented as an integral following a suggestion of Klauder.[8] The integral is approxi-

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[1] M. Lax and J. C. Phillips, Phys. Rev. **110**, 41 (1958); H. Frisch and S. Lloyd, *ibid.* **120**, 1175 (1960); J. R. Klauder, Ann. Phys. (N.Y.) **14**, 43 (1961). For a closely related problem see also F. J. Dyson, Phys. Rev. **92**, 1331 (1953).

[2] R. H. Parmenter, Phys. Rev. **97**, 587 (1955); **104**, 22 (1956).

[3] P. A. Wolff, Phys. Rev. **126**, 405 (1962).

[4] V. L. Bonch-Bruevich and A. G. Mironov, Fiz. Tverd. Tela, **3**, 3009 [translation: Soviet Phys.—Solid State **3**, 2194 (1962)].

[5] V. L. Bonch-Bruevich, in *Proceedings of the International Conference on the Physics of Semiconductors at Exeter, July, 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 216.

[6] L. V. Keldysh, paper presented at the Exeter Conference but not in the Proceedings.

[7] E. O. Kane, in *Proceedings of the International Conference on the Physics of Semiconductors at Exeter, July, 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 252.

[8] J. R. Klauder (private communication).

mated by the method of stationary phase plus an additional expansion of the exponent as a power series in the potential. To lowest order, the distribution is also Gaussian about the average potential with a half-width 2.1 times greater than that obtained by the uniform cluster approximation. The effect of the kinetic energy of localization, which is ignored in the Thomas-Fermi method, is to cause an averaging or "motional narrowing" effect to occur which will reduce the half-width to a value closer to that given by the uniform cluster method.

In Sec. IV the effect of density-of-state tails on the *I-V* characteristic of tunnel junctions is discussed. The semiclassical approach is also used here so that tunneling in the "band tails" is viewed as ordinary tunneling from localized regions of abnormally low-potential energy. A number of further approximations are required to obtain numerical results. Comparison with experimental results on silicon obtained by Logan *et al.*[9] is made. The agreement is quite satisfactory.

II. MODEL HAMILTONIAN

We assume the following model Hamiltonian:

$$H=H_0+H_1, \tag{1}$$

$$H_1=\sum_i v(r-r_i)-\mathcal{V}_0, \tag{2}$$

$$v(r)=\frac{e^2}{\epsilon_d r}\exp(-\kappa_D r), \tag{3}$$

$$H_0=(p^2/2m^*)+C. \tag{4}$$

We treat the perfect solid by an effective mass m^* and dielectric constant ϵ_d. The impurities are represented by screened Coulomb potentials, Eq. (3), which are randomly distributed over lattice sites, r_i, with average density n. $\mathcal{V}_0$ is a constant chosen so that the average perturbing potential is zero. The reciprocal screening length, κ_D, is given by the Thomas-Fermi model[3,10] as

$$\begin{aligned}\kappa_D&=2n^{1/6}(3/\pi)^{1/6}a_0^{*-1/2},\\ a_0^*&=\epsilon_d\hbar^2/m^*e^2.\end{aligned} \tag{5}$$

The number of particles, ν, in a Debye sphere $(4\pi/3)\kappa_D^{-3}$, is given by

$$\nu=(\pi/3)^{3/2}n^{1/2}a_0^{*3/2}/2. \tag{6}$$

The range of validity of Eq. (5) is $\nu\gg1$. For values of ν much smaller than 1, screening is due to electrons in localized orbitals. Although we use Eqs. (5) and (6) down to $\nu<1$ it should be emphasized that the formula is quantitatively accurate only for large ν. It would be desirable to allow κ_D to be a function of the local impurity density rather than only the average density but we have not considered this possibility. The model Hamiltonian of Eqs. (1) through (4) has been justified by Wolff[3] in the high density or large ν limit. Our definition of $\mathcal{V}_0$, which corresponds to zero average potential, is a mathematical convenience. The constant C, in Eq. (4), depends on the correlation energy of the electron gas as shown by Wolff.[3] In what follows we set $C=0$.

III. "UNIFORM CLUSTER" APPROXIMATION

In this section we study the model Hamitonian of Eqs. (1) through (4) from a very simple point of view. Although the assumptions made are rather crude, they retain the essential features of the problem. In the next section a more quantitative approach is attempted, using the results of this section as a guide.

Our point of view is that some cluster of m atoms in a volume w is most important in producing any fluctuations of interest. We consider this cluster embedded in a uniform background of average density. The deviation from the average potential [taken as zero according to Eq. (2)] is taken to be the uniform average of the potential over the volume, w, multiplied by the excess of the number m over the average number nw

$$\mathcal{V}=(m-nw)\int_w v(\mathbf{r}_1-\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2/w^2. \tag{7}$$

The kinetic energy, E_{loc}, of the lowest state of an electron in a spherical box of radius r_w is

$$E_{\text{loc}}=(\pi^2/2r_w^2)(\hbar^2/m^*). \tag{8}$$

We take the formula for the density of states for a large volume

$$\begin{aligned}\rho(E)&=\frac{(2)^{1/2}m^{*3/2}}{\pi^2\hbar^3}(E-\mathcal{V})^{1/2}w; && E-\mathcal{V}\geq0.84E_{\text{loc}},\\ &=0; && E-\mathcal{V}<0.84E_{\text{loc}}.\end{aligned} \tag{9}$$

With this rather arbitrary cutoff choice,

$$\int_{-\infty}^{E_{loc}} d(E-\mathcal{V})\rho(E)=(1/2)2=1.$$

In Eq. (9) we include a factor 2 for spin.

The probability of finding m atoms in the volume w is given by the Poisson distribution formula

$$P(m,w)=\frac{(nw)^m}{m!}e^{-nw}. \tag{10}$$

In all our calculations we will assume that the impurity ions are randomly distributed. A better approximation would be to compute the total electrostatic energy of a given cluster, $E_{\text{fluct}}(T_{\text{eff}})$, and multiply the

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[9] R. A. Logan and A. G. Chynoweth, following paper, Phys. Rev. **131**, 89 (1963).

[10] R. B. Dingle, Phil. Mag. **46**, 831 (1955).

probability, $P(m,w)$, computed on the random hypothesis by a factor $\exp\{-E_{\text{fluct}}(T_{\text{eff}})/kT_{\text{eff}}\}$ where T_{eff} is an effective temperature at which the ions become "frozen in." This factor is probably significant in many cases of practical interest. An experimental test of its significance would be a dependence of any phenomena associated with band tailing on the rate of annealing. $P(m,w)$ satisfies the normalization condition

$$\sum_{m=0}^{\infty} P(m,w)=1. \tag{11}$$

The over-all density of states is then given by

$$\rho(E)=\frac{\sqrt{2}m^{*3/2}}{\pi^2\hbar^3}V\int[E-\mathcal{V}(m,w)]^{1/2}P(m,w)dm;$$
$$E-\mathcal{V}\geq 0.84E_{\text{loc}}. \tag{12}$$

We have converted the sum in Eq. (11) to an integral, treating m as a continuous variable. A factor V/w for the number of clusters in the volume, V, has been included. We choose w to maximize the number of states below the average potential

$$M_0(0)=\int_{-\infty}^{0}\rho(E)dE. \tag{13}$$

By considering fluctuations over a given volume, w, we are clearly underestimating the total effect since fluctuations over all possible volumes actually occur. We attempt to minimize our error by selecting the single volume, w, for which density fluctuations contribute most strongly to the density of states. The method for choosing w is somewhat arbitrary but we feel that maximizing $M_0(0)$ as a function of w is a reasonable criterion. Inserting (12) in (13) we have,

$$M_0(0)=\frac{2(2)^{1/2}m^{*3/2}}{3\pi^2\hbar^3}V\int[(-\mathcal{V})^{3/2}$$
$$-(0.84E_{\text{loc}})^{3/2}]P(m,w)dm;$$
$$-\mathcal{V}>0.84E_{\text{loc}}. \tag{14}$$

With the use of Stirling's approximation for $m!$, we may write Eq. (10) in the form

$$P(m,w)\simeq\frac{1}{(2\pi m)^{1/2}}e^{\Phi}, \tag{15}$$

$$\Phi\equiv m-nw+m(\ln nw-\ln m), \tag{16}$$

where Φ has its maximal value, 0, at the point $m=nw$. Expanding about this point we may write

$$P(m,w)\simeq\frac{1}{(2\pi nw)^{1/2}}e^{-(m-nw)^2/2nw}. \tag{17}$$

This expansion is valid for $m-nw\ll nw$. If we substitute (17) in (14) and ignore the localization energy E_{loc}, Eq. (14) may be written

$$M_0(0)=\frac{2^{5/4}\Gamma(5/4)m^{*3/2}V}{3\pi^{5/2}\hbar^3}(nw)^{3/4}K^{3/2}(\kappa_D r_w), \tag{18}$$

$$K\equiv-\int_w v(\mathbf{r}_1-\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2/w^2, \tag{19}$$

$$K=(9e^2/2\epsilon_d)\kappa_D(\kappa_D r_w)^{-6}\{\tfrac{2}{3}(\kappa_D r_w)^3$$
$$-(\kappa_D r_w)^2+1-(1+\kappa_D r_w)^2e^{-2\kappa_D r_w}\}, \tag{20}$$

$$w\equiv(4\pi/3)r_w^3, \tag{21}$$

where (20) has been evaluated for the screened Coulomb potential. The function on the right of Eq. (20) has a broad maximum whose peak is at $\kappa_D r_w=0.7$. Using this optimum value, together with Eq. (7), we may write Eq. (17) as

$$P(m,w)=\frac{1}{(2\pi nw)^{1/2}}\exp\left\{\frac{-\kappa_D\epsilon_d^2\mathcal{V}^2}{2.8ne^4}\right\}. \tag{22}$$

Substituting $\kappa_D r_w=0.7$ in Eq. (8) gives

$$E_{\text{loc}}=1.0\kappa_D^2\hbar^2/m^*. \tag{23}$$

Defining an energy scale factor η' by Eq. (22),

$$\eta'\equiv(2.8n/\kappa_D)^{1/2}(e^2/\epsilon_d), \tag{24}$$

we find, using Eqs. (5) and (23)

$$\eta'/0.84E_{\text{loc}}=n^{1/12}a_0^{*1/4}/2.8. \tag{25}$$

According to Eqs. (25) and (12), the kinetic energy of localization has a significant effect on the density-of-states problem for the concentration range of interest, $n\sim 0.01$ to 10^4. It could be included as suggested in Eq. (14), determining a new optimum w. The optimum w would naturally increase to reduce the localization energy. The increase in cluster size would then reduce the fluctuations and narrow the distribution. No drastic changes are expected in view of the fact that $M_0(0)$ has a broad maximum as a function of w.

For states far below the average potential, $m-nw\gg nw$, and the expansion of φ leading to Eq. (17) is invalid. In this range φ depends principally on m so that, for maximum φ, m should be as small as possible, consistent with Eq. (7). This evidently demands w small so that K in Eqs. (19) and (20) is large. However, w cannot become arbitrarily small on account of the kinetic energy of localization.

We now pick w to maximize $\rho(E)$. We could have used this procedure in place of maximizing $M_0(0)$ in Eq. (14). However, we would then have no guarantee of a properly normalized $P(m,w)$. States far below the average potential contribute so little to the probability normalization that no problem arises.

In the limit $\kappa_D r_w \ll 1$, Eq. (20) reduces to

$$K = 1.2e^2/\epsilon_d r_w, \quad \kappa_D r_w \ll 1. \tag{26}$$

The most important factor determining $\rho(E)$ in Eq. (12) for large $|E|$ is $P(m,w)$. To find the optimum w we maximize Φ in Eq. (16), neglecting the average number nw compared to m. m is evaluated at $E-\mathcal{V}=0.84E_{\text{loc}}$. The maximum in Φ then occurs for $dm/dr_w=0$.

$$r_w = 2.0\hbar/(m^{*1/2}|E|^{1/2}), \tag{27}$$

$$m = 3.4|E|^{1/2}\epsilon_d\hbar/(e^2 m^{*1/2}). \tag{28}$$

Substituting (27) and (28) in Eq. (16), expanding Φ to first order in Δm about the maximum and taking the square root in Eq. (12) as a constant $=(0.84E_{\text{loc}})^{1/2}$, we find the approximate result

$$\rho(E) \simeq \frac{m^{*3/2}}{\hbar^3}\left(\frac{|E|}{\pi m}\right)^{1/2}\frac{V}{\pi^2}\left(\frac{nwe}{m}\right)^m \frac{e^{-nw}}{\ln(m/nw)}, \tag{29}$$

$$w = 1.3\times 10^3 a_0^{*3}/m^3,$$

with m given by Eq. (28).

In summary, we have estimated the effects of fluctuations for two energy regions. Near the average potential the important fluctuations take place in a volume of the order of a Debye sphere, $(4\pi/3)\kappa_D^{-3}$. The density of states is approximated by Eqs. (12) and (22). At very low energies, the important fluctuations occur for very much smaller volumes. The density of states is then given by Eq. (29). The fluctuations represented by Eq. (22) involve only the potential and, hence, produce "tails" on both band edges. On the other hand, the highly localized clusters represented by Eq. (29) are important only for majority carriers which are bound to such regions, whereas minority carriers are repelled.

IV. THOMAS-FERMI METHOD

In this section we refine the treatment of the previous section to take more accurate account of the fluctuations in the potential. We still treat the kinetic energy in the approximate manner characteristic of the Thomas-Fermi method. The assumption is made that the potential is sufficiently slowly varying that one can define a "local" density of states using the formula appropriate to a large volume.

$$\Delta\rho(E) = \sqrt{2}m^{*3/2}\Delta V(E-\mathcal{V})^{1/2}/\pi^2\hbar^3. \tag{30}$$

Equation (25) of Sec. III shows that this approximation is never well satisfied.

We define the potential distribution function, $F(\mathcal{V})$, by

$$\Delta p = F(\mathcal{V})\Delta\mathcal{V}, \tag{31}$$

where Δp is the probability of finding the potential between $\mathcal{V}$ and $\mathcal{V}+\Delta\mathcal{V}$. The total density of states is then simply

$$\rho(E) = \frac{\sqrt{2}m^{*3/2}V}{\pi^2\hbar^3}\int_{-\infty}^{E}(E-\mathcal{V})^{1/2}F(\mathcal{V})d\mathcal{V}. \tag{32}$$

We can write the distribution function $F(\mathcal{V})$ as an integral using a method due to Klauder.[8] From the definition

$$F(\mathcal{V}) = \lim_{\substack{m\to\infty \\ m=nV}} \int \delta\{\mathcal{V}+\mathcal{V}_0-\sum_{i=1}^{m} v(r_i)\} \times d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_m/V^m, \tag{33}$$

where n is the average impurity density. Expanding the δ function in a Fourier series gives

$$F(\mathcal{V}) = \lim_{\substack{m\to\infty \\ m=nV}} \frac{1}{2\pi}\int d\alpha \exp\{i\alpha[\mathcal{V}+\mathcal{V}_0-\sum_{i=1}^{m} v(\mathbf{r}_i)]\} \times d\mathbf{r}_1\cdots d\mathbf{r}_m/V^m. \tag{34}$$

We then write

$$\int_V e^{-i\alpha v(\mathbf{r})}d\mathbf{r}/V = 1+\int_V (e^{-i\alpha v(\mathbf{r})}-1)d\mathbf{r}/V. \tag{35}$$

If $v(\mathbf{r})$ tends to zero sufficiently rapidly, the integral on the right of Eq. (35) becomes infinitesimal for large V. Using

$$\lim_{V\to\infty}(1+a/V)^{nV} = e^{an},$$

we obtain

$$F(\mathcal{V}) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\alpha \exp\left\{i\alpha(\mathcal{V}+\mathcal{V}_0) + n\int [e^{-i\alpha v(\mathbf{r})}-1]d\mathbf{r}\right\}. \tag{36}$$

Equation (36) is Klauder's result.

Equation (36) is only well defined for well-behaved potentials $v(r)$. In order to make the screened Coulomb potential well behaved, we can introduce a cutoff parameter, r_0, and replace the divergent r^{-1} factor by $(r+r_0)^{-1}$. We discuss this point more fully later on.

In the limit of large n, the integral in Eq. (36) may be evaluated using the method of stationary phase.[11]

$$\varphi \equiv i\alpha(\mathcal{V}+\mathcal{V}_0)+n\int [e^{-i\alpha v(r)}-1]d\mathbf{r}, \tag{37}$$

$$\frac{d\varphi}{d\alpha} = i(\mathcal{V}+\mathcal{V}_0)-in\int v(\mathbf{r})e^{-i\alpha v(\mathbf{r})}d\mathbf{r}, \tag{38}$$

$$\frac{d^2\varphi}{d\alpha^2} = -n\int v^2(r)e^{-i\alpha v(\mathbf{r})}d\mathbf{r}. \tag{39}$$

If α_i are the solutions of $d\varphi/d\alpha=0$ and $\varphi_i\equiv\varphi(\alpha_i)$, $\varphi_i''\equiv(d^2\varphi/d\alpha^2)_{\alpha_i}$, the method of stationary phase gives

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[11] The author thanks D. Arnush for assistance in the evaluation of Eq. (36).

for $F(\mathcal{V})$ in Eq. (36)

$$F(\mathcal{V})=\sum_i e^{\varphi_i}/(-2\pi\varphi_i'')^{1/2}. \tag{40}$$

One point of stationary phase is easily found, assuming α small and expanding the exponentials in powers of α. (The contribution of other possible points of stationary phase is unclear. The example treated in the Appendix suggests that they are not too important.)

$$0=\frac{d\varphi_i}{d\alpha}=i\mathcal{V}-in\sum_{m=1}^{\infty}\frac{(-i\alpha)^m}{m!}\int v^{m+1}(r)d\mathbf{r}, \tag{41}$$

$$\varphi_i=-n\sum_{m=2}^{\infty}\frac{(-i\alpha)^m(m-1)}{m!}\int v^m(r)d\mathbf{r}, \tag{42}$$

$$\varphi_i''=-n\sum_{m=0}^{\infty}\frac{(-i\alpha)^m}{m!}\int v^{m+2}(r)d\mathbf{r}. \tag{43}$$

We have used

$$\mathcal{V}_0=n\int v(r)d\mathbf{r}, \tag{44}$$

in keeping with the definition that the perturbing potential have zero-average value. Equation (41) has been used to eliminate $\mathcal{V}$ in Eq. (37) to give (42).

The series expansion in α in Eq. (41) may be inverted to give α as a power series in $\mathcal{V}$. The result is then substituted in (42) and (43) to give φ_i and φ_i'' as a power series in $\mathcal{V}$.

$$\varphi_i=-n\left\{\frac{\mathcal{V}^2}{2n^2\int v^2(r)d\mathbf{r}}-\frac{\mathcal{V}^3\int v^3(r)d\mathbf{r}}{6n^3\left(\int v^2(r)d\mathbf{r}\right)^3}+\frac{\mathcal{V}^4}{n^4}\left[-\frac{1}{24}\frac{\int v^4(r)d\mathbf{r}}{\left(\int v^2(r)d\mathbf{r}\right)^4}+\frac{\left(\int v^3(r)d\mathbf{r}\right)^2}{8\left(\int v^2(r)d\mathbf{r}\right)^5}\right]+\cdots\right\}, \tag{45}$$

$$\varphi_i''=-n\int v^2(r)d\mathbf{r}+\cdots. \tag{46}$$

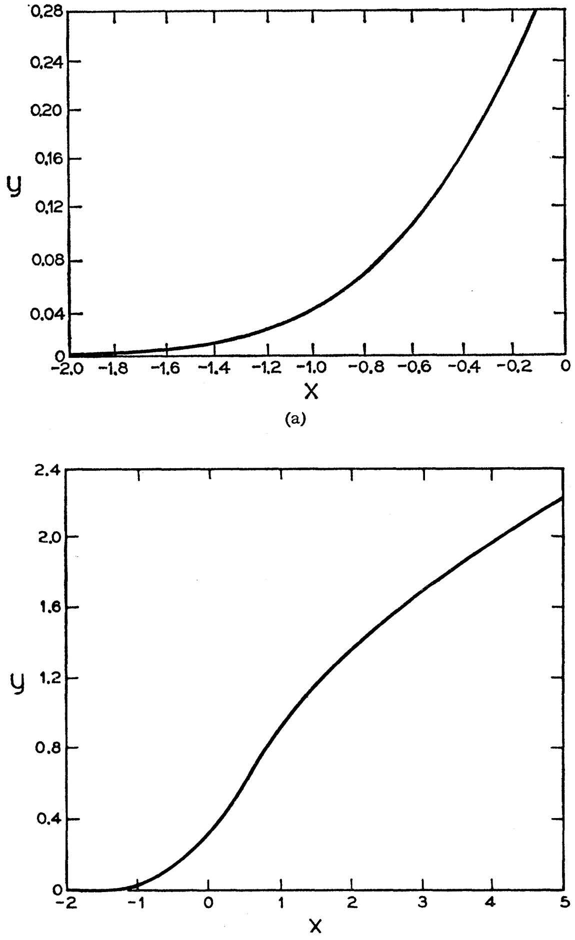
Taking just the leading term in (45) and (46), we obtain from (40)

$$F(\mathcal{V})=(1/(\pi)^{1/2}\eta)\exp(-\mathcal{V}^2/\eta^2), \tag{47}$$
$$\eta\equiv(e^2/\epsilon_d)(4\pi n/\kappa_D)^{1/2},$$

where we have used

$$\int v^2(r)d\mathbf{r}=2\pi e^4/\epsilon_d^2\kappa_D \tag{48}$$

for the screened Coulomb potential.



(b)

FIG. 1. (a),(b). Thomas-Fermi density of states versus energy in dimensionless variables.

The Thomas-Fermi density of states is then found by substituting Eq. (47) in Eq. (32). Using dimensionless variables, we can express the results in terms of a function $y(x)$ with no parameters.

$$\rho(E)=y(E/\eta)m^{*3/2}(2\eta)^{1/2}V\pi^{-2}\hbar^{-3}, \tag{48a}$$

$$y(x)=\pi^{-1/2}\int_{-\infty}^{x}(x-\zeta)^{1/2}\exp(-\zeta^2)d\zeta, \tag{48b}$$

$y(x)$ is plotted in Fig. 1. It is clear from Eq. (48b) that $\rho\sim E^{1/2}$ at high energies and $\rho\sim\exp(-E^2/\eta^2)$ at low energies.

It is of interest to compare Eq. (47) with Eq. (22) of Sec. III. Comparing Eqs. (32) and (12) and using (7) and (19), we find

$$F(\mathcal{V})=P(m,w)/K. \tag{49}$$

For the optimum w, $\kappa_D r_w=0.7$

$$P(m,w)/K=(2.1/\pi^{1/2}\eta)\exp[-(2.1\mathcal{V}/\eta)^2]. \tag{50}$$

The similarity of Eqs. (50) and (47) demonstrates that (47) results from clusters whose size is of the order of the Debye sphere, $4\pi/(3\kappa_D^3)$. The more accurate result, Eq. (47), is seen to give a distribution broader by a factor 2.1 than the crude estimate of Eq. (50). One would expect Eq. (47) to give a broader distribution than Eq. (50) due to the effect of "fluctuations within fluctuations" which are ignored in deriving Eq. (50).

We have seen in Eq. (25) that the energy of localization is a significant effect, not properly accounted for by the Thomas-Fermi method. The nonlocalizability results in an averaging over the smaller scale fluctuations and a consequent narrowing of the density of states distribution. Hence, the best effective distribution probably lies somewhere between those of Eqs. (47) and (50). Kinetic energy (motional) narrowing of the distribution function will also affect Eq. (50), though to a lesser degree. This could be estimated in the manner suggested in Sec. III. A further narrowing effect which we have not considered is that κ_D should really be a function of the local rather than the average density. This should not be a large effect, however.

We may also estimate the range of validity of Eq. (47) by considering the ratio of the neglected terms in (45).

$$\frac{\varphi_i^{(3)}}{\varphi_i^{(2)}}=-\frac{\mathcal{V}}{3n}\frac{\int v^3(r)d\mathbf{r}}{\left(\int v^2(r)dr\right)^2}, \tag{51}$$

$$\frac{\varphi_i^{(4)}}{\varphi_i^{(2)}}=-\frac{\mathcal{V}^2}{12n^2}\frac{\int v^4(r)d\mathbf{r}}{\left(\int v^2(r)d\mathbf{r}\right)^4}+\frac{9}{4}\left(\frac{\varphi_i^{(3)}}{\varphi_i^{(2)}}\right)^2. \tag{52}$$

The superscript on φ denotes the power of $\mathcal{V}$.

If the screened Coulomb interaction is substituted in $\int v^3$ and $\int v^4$ the integrals are seen to diverge. We therefore introduce a "cutoff" parameter r_0 and write

$$v(r)=-\frac{e^2}{\epsilon_d(r+r_0)}\exp(-\kappa_D r). \tag{53}$$

This device obviously de-emphasizes the contribution to the distribution function from very close impurities. These small distance contributions are, in fact, important for energy states very far below the average potential, as we have seen in Sec. III. In determining these contributions it is essential to take proper account of the kinetic energy of localization. We have no way here of improving on the estimate made in Sec. III. Equation (47) is only useful for computing the fluctuations due to clusters of the size of the Debye volume. Hence, we take r_0 as large as possible but still sufficiently less than κ_D^{-1} so that Eq. (48) is not seriously altered.

We then get the rough estimates

$$\begin{aligned}&\int v^3(\mathbf{r})d\mathbf{r}\simeq 4\pi(e^2/\epsilon_d)^3,\\&\int v^4(r)d\mathbf{r}\simeq(4\pi/3r_0)(e^2/\epsilon_d)^4,\end{aligned} \tag{54}$$

$$\varphi^{(3)}/\varphi^{(2)}\simeq-(\mathcal{V}\kappa_D^2/3\pi n)(\epsilon_d/e^2), \tag{55}$$

$$\varphi^{(4)}/\varphi^{(2)}\simeq(\mathcal{V}^2\kappa_D^4/144n^2\pi^4r_0)(\epsilon_d^2a_0^*/e^4). \tag{56}$$

For all densities of interest, Eq. (55) is the more stringent condition. Using $\mathcal{V}=\eta$ as suggested by Eq. (47), we have

$$\varphi^{(3)}/\varphi^{(2)}\simeq-4/(3\pi^{1/2}n^{1/3}a_0^*). \tag{57}$$

Although Eq. (57) is not well satisfied in the range $n=0.01$ to 10^4, it is evidently better satisfied at large n than the localization condition of Eq. (25); hence, the latter remains the most serious limitation on the accuracy of these results for large n.

We should also inquire how accurate the approximation of stationary phase itself may be. In the Appendix, the method of stationary phase applied to a simple soluble problem is found to be equivalent to using Stirling's approximation for $m!$ in the exact solution where m is the number of atoms (square wells) contributing to the potential. Since Stirling's approximation is only 8% in error for $m=1$ and less for $m>1$, this is not serious by our standards. The number of atoms in a Debye sphere is given by Eq. (6).

V. BAND-TAIL TUNNELING IN THE SEMICLASSICAL APPROXIMATION

In calculating the effect of density of states tails on the *I*-*V* characteristic of a tunnel junction, we use a semiclassical approach. We assume, as in Sec. III, that electrons can be localized within a volume w, and that their distribution in energy is given by the usual treatment for a box with periodic boundary conditions. We take the box to be a cube for simplicity.

We then divide all space into cubes of volume w, which we take to be the "correlation" volume for the potential. We oversimplify the correlation problem by assuming the potential constant within a given cube and uncorrelated between different cubes. We also consider a division of all space into one-dimensional arrays of cubes along the direction of the junction field. We consider the tunneling electrons to progress along this array and we assume that different arrays make independent parallel contributions to the tunneling current. Hereafter we focus our attention on the contribution of a single array.

We will assume a constant field model for the junction and ignore all fluctuation effects in the junction itself.

We then consider the contribution to the tunnel current, for a cube at a distance x_1 from the junction edge, due to electrons of energy, E. The definition of symbols is shown in Fig. 2. The probability dp of finding the potential at the value, $\mathcal{V}$ is

$$dp = F(\mathcal{V})d\mathcal{V}dx/w^{1/3}, \tag{58}$$

where $F(\mathcal{V})$, the potential distribution function, is defined in Eq. (31) of Sec. IV. Equation (58) is valid only in the limit $dx \gg w^{1/3}$ which implies that $w^{1/3}$ is much smaller than all other lengths of interest in our problem. This is not the case but we make the approximation for reasons of simplicity so that x can be treated as a continuous variable.[12]

We assume the kinetic energy of motion perpendicular to the junction field, $E_\perp$, to be a constant of the motion. The total tunnel current is then given by the expression

$$J = A\int_{E_{F2}}^{E_{F1}} dE\, S_1 S_2 e^{-\lambda_0}, \tag{59}$$

$$\begin{aligned} S_1 &= \int_0^\infty dE_{\perp 1}\int_0^\infty (dx_1/w_1^{1/3}) \\ &\qquad \times \int_{-\infty}^{\epsilon_1} d\mathcal{V}_1\, \mathcal{P}_1 e^{-2\kappa_1 \tilde{x}_1 - \lambda_1}, \\ S_2 &= \int_{-\infty}^0 dE_{\perp 2}\int_0^\infty (dx_2/w_2^{1/3}) \\ &\qquad \times \int_{-\epsilon_2}^{\infty} d\mathcal{V}_2\, \mathcal{P}_{2,} e^{-2\kappa_2 \tilde{x}_2 - \lambda_2}, \end{aligned} \tag{60}$$

$$\begin{aligned} \epsilon_1 &\equiv E - E_{\perp 1} - E_1, \\ \epsilon_2 &\equiv E_{\perp 2} + E_2 - E, \end{aligned} \tag{61}$$

$$\begin{aligned} \tilde{x} &\equiv |x|, & x<0 \\ &\equiv 0, & x>0, \end{aligned} \tag{62}$$

$$\hbar^2\kappa_1^2/2|m_i^*| = \tilde{\epsilon}_i; \qquad i=1,2 \tag{63}$$

$$E_{\perp i} = \hbar^2 k_\perp^2/2m_i^*; \quad i=1,2. \tag{64}$$

The prefactor A and the integrals $\int dE dE_{\perp 1} dE_{\perp 2}$ are the same as for indirect tunneling with the perfect crystal band structure.[13] The integrals arise from density-of-states factors.

The integration over x_1 contains a factor $\exp(-2\kappa_1 \tilde{x}_1)$ which is the tunneling attenuation factor for the electron to tunnel from the point x_1 to the junction. The attenuation in traversing the junction is included separately in the factor $\exp(-\lambda_0-\lambda_1-\lambda_2)$. The additional attenuation, $\exp(-2\kappa_1 \tilde{x}_1)$, is computed with respect to the averaged band edge, E_1, as given by Eq. (63), which represents a further approximation since it is really $\exp(-2\kappa x)$ which should be averaged over the potential fluctuations.

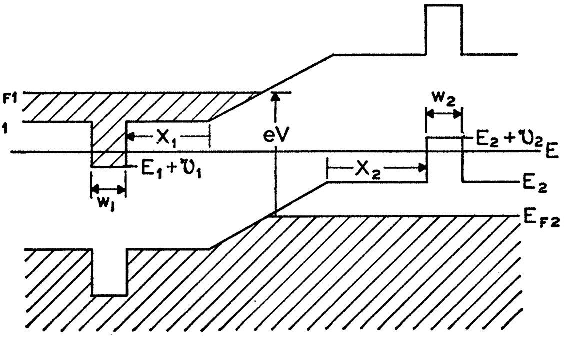


FIG. 2. Definition of symbols used in calculating I-V characteristic of tunnel junction.

The factor $\mathcal{P}_1$, given by

$$\begin{aligned} \mathcal{P}_1 &\equiv F_1(\mathcal{V}_1)\exp\left\{-\left(\int_{-\infty}^{\epsilon_1} F_1(\mathcal{V}_1)d\mathcal{V}_1\right)x_1/w_1^{1/3}\right\}, \\ \mathcal{P}_2 &\equiv F_2(\mathcal{V}_2)\exp\left\{-\left(\int_{-\epsilon_2}^{\infty} F_2(\mathcal{V}_2)d\mathcal{V}_2\right)x_2/w_2^{1/3}\right\}, \end{aligned} \tag{65}$$

gives the probability of finding the potential at $\mathcal{V}_1$ at the point x_1 and of not finding the potential below ϵ_1 between 0 and x_1. The band edge, E_1, is taken as the value for the average potential. The exponential factor in Eq. (65) is essential to avoid overestimating the current. The electron is to be counted as tunneling from the *first* cube in which the potential is sufficiently low for a real state to exist. We assume that w is large enough that we can ignore the discrete character of the quantum states.

The tunneling attenuation factors can be easily shown to have the form

$$\begin{aligned} \lambda_1 &\equiv +(E_{\perp 1}/\bar{E}_\perp) - 4(2m_{1x}^*)^{1/2}\tilde{\epsilon}_1^{3/2}/3F\hbar, \\ \lambda_2 &\equiv -(E_{\perp 2}/\bar{E}_\perp) - 4(2|m_{2x}^*|)^{1/2}\tilde{\epsilon}_2^{3/2}/3F\hbar, \end{aligned} \tag{66}$$

$$\begin{aligned} \bar{E}_\perp &\equiv \hbar F/(2\sqrt{2} m_{rx}^{*1/2} E_G^{1/2}), \\ \lambda_0 &= 4(2m_{rx}^*)^{1/2} E_G^{3/2}/(3\hbar F), \\ m_{rx}^{*-1} &= m_{1x}^{*-1} + |m_{2x}^*|^{-1}. \end{aligned} \tag{67}$$

F is the constant *force* on the electron in the junction, assumed positive. λ_0 is the attenuation exponent for an electron with $E_{\perp 1} = E_{\perp 2} = 0$ with classical turning points in the junction region. λ_1 and λ_2 contain the additional effects of the perpendicular energy and the correction due to the fact that the electron may enter the junction at a point where its x-kinetic energy, $\hbar^2 k_x^2/2m_{1x}^*$, is already negative. This happens whenever ϵ_1 is negative. This latter effect reduces the amount of tunneling attenuation in the junction region.

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[12] Although the transition to continuous x appears to be a further approximation, in a sense it is an improvement since the correlation boxes should be randomly located. The continuous variable assumption does not properly treat the correlation problem however, which demands no change of potential over distance $\ll w^{1/3}$.

[13] E. O. Kane, J. Appl. Phys. 32, 83 (1961).

The integrals over dx_i and $d\mathcal{V}_i$ in Eqs. (59) and (60) are easily performed

$$S_1(E-E_1)=\int_{-\infty}^{E-E_1} d\epsilon_1 \frac{\mathrm{Erfc}(-\epsilon_1/\eta_1)e^{-\lambda_1}}{2(\pi)^{1/2}\kappa_1 w_1{}^{1/3}+\mathrm{Erfc}(-\epsilon_1/\eta_1)}$$
$$S_2(E_2-E)=\int_{-\infty}^{E_2-E} d\epsilon_2 \frac{\mathrm{Erfc}(-\epsilon_2/\eta_2)e^{-\lambda_2}}{2(\pi)^{1/2}\kappa_2 w_2{}^{1/3}+\mathrm{Erfc}(-\epsilon_2/\eta_2)}, \tag{68}$$

$$J=A\int_{E_{F2}}^{E_{F1}} dES_1(E-E_1)S_2(E_2-E)e^{-\lambda_0}. \tag{69}$$

In evaluating (68) we have used

$$F(\mathcal{V})=(1/\pi^{1/2}\eta)\exp(-\mathcal{V}^2/\eta^2) \tag{70}$$

in agreement with Eq. (47). We have also made a change of the variable of integration from $dE_\perp$ to $d\epsilon$ using Eq. (61). When ϵ is positive in the integrands of Eq. (68) the fractional factors become unity because $\kappa=0$ according to Eqs. (62) and (63). The second term on the right of Eq. (66) is also zero. The contribution to the tunnel current is just that of the perfect crystal band structure for the case of indirect tunneling. The sharp division at $\epsilon=0$ between contributions from "band tails" and contributions from "perfect bands" is, of course, an oversimplification which results from taking an average κ rather than averaging over $e^{-2\kappa x}$. The function S is easily computed but it is a function of too many parameters to tabulate. We define a new function closely related to S

$$\mathcal{S}(x)=\int_{-\infty}^{x} dx'\frac{\mathrm{Erfc}(-x')\exp\{b\tilde{x}'^{3/2}+cx'\}}{a\tilde{x}'^{1/2}+\mathrm{Erfc}(-x')}, \tag{71}$$

$$J=A\eta_1\eta_2\exp\{-\lambda_0(V)+(eV-\zeta_1-\zeta_2)/\bar{E}_\perp\}$$
$$\times\int_0^{eV} dE\,\mathcal{S}_1\left(\frac{E-eV+\zeta_1}{\eta_1}\right)\mathcal{S}_2\left(\frac{\zeta_2-E}{\eta_2}\right), \tag{72}$$

$$j\equiv J/(Ae^{-\lambda_0(0)}),$$
$$\zeta_i=|E_{F_i}-E_i|,$$
$$a_i=2w_i{}^{1/3}(2\pi\eta_i|m_{ix}{}^*|)^{1/2}/\hbar, \tag{73}$$
$$b_i=4(2|m_{ix}{}^*|)^{1/2}\eta_i{}^{3/2}/3F\hbar,$$
$$c_i=\eta_i/\bar{E}_\perp.$$

In deriving Eq. (72) we have used $E_{F1}=E_1+\zeta_1=E_{F2}+eV$ where eV is positive for forward bias. We have also chosen an energy zero $E_{F2}=E_2-\zeta_2=0$.

In Figs. 3 and 4 we show $\mathcal{S}_1(x)$, $\mathcal{S}_2(x)$, and $j(V)$ for a choice of parameters appropriate to silicon doped with $n_A=2.3\times10^{19}$ acceptors and $n_D=4.8\times10^{19}$ donors forming an abrupt junction. The field is taken as $\frac{2}{3}$ times the maximum field. The value $\frac{2}{3}$ is appropriate for an abrupt junction where the point of stationary phase, $\kappa_{x1}=\kappa_{x2}$, occurs at the same point as the maximum field. This requires the condition $m_{2x}{}^*/m_{1x}{}^*=n_A/n_D$, which is nearly satisfied for the above doping.

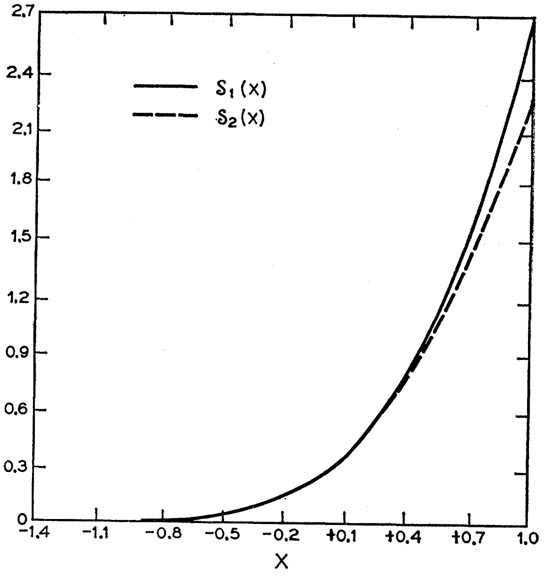

FIG. 3. $\mathcal{S}_1(x)$, $\mathcal{S}_2(x)$ as defined in Eqs. (71) and (73) for silicon with $n_A=2.3\times10^{19}$/cc, $n_D=4.8\times10^{19}$/cc.

The appropriate tunneling masses are taken as the ellipsoidal mass in the [111] direction for the electrons and the light hole mass for the holes. This gives $m_{1x}{}^*=0.26m_0$, $m_{2x}{}^*=0.16m_0$. We have assumed the junction plane to have a [111] orientation. We calculate $\bar{E}_\perp=0.047$ eV.

We allow for the voltage dependence of $\lambda_0(V)$ to first order

$$\lambda_0(V)\simeq\lambda_0(0)+(\partial\lambda_0/\partial V)V.$$

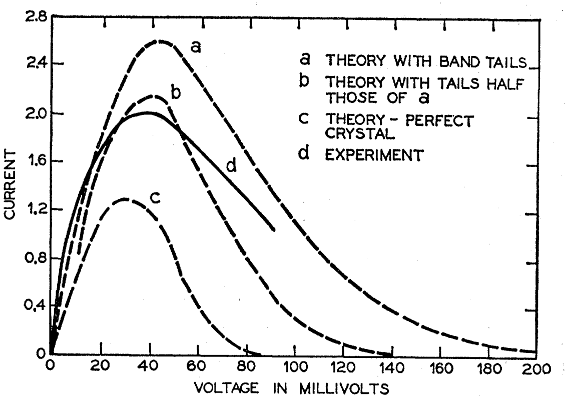

FIG. 4. (a) Theoretical $j(V)$ for silicon with $n_A=2.3\times10^{19}$/cc, $n_D=4.8\times10^{19}$/cc with η given by Eq. (47). (b) Theoretical $j(V)$ for the same parameters as in (a) except that η's are taken as $\frac{1}{2}$ the value given by Eq. (47). (c) Theoretical $j(V)$ with the same doping as in (a) for the perfect crystal band structure, $\lim\eta\rightarrow0$. (d) Experimentally determined $j(V)$ for silicon with $n_A=2.3\times10^{19}$/cc, $n_D=4.8\times10^{19}$/cc.

Using Eq. (67) together with $\partial F/\partial V=-F/2V_0$ for an

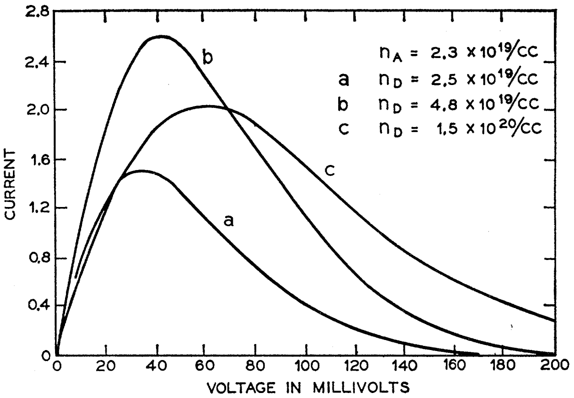

FIG. 5. Theoretical characteristic for a range of donor concentrations. Tails given by Eq. (47).

abrupt junction, we calculate $\partial\lambda_0/\partial V = 6.5$ volts^{-1}. V_0 is the total potential change across the junction, $V_0 = E_G + \zeta_1 + \zeta_2$.

We compute the Gaussian width η, using Eq. (47). The appropriate mass in these formulas is the density-of-states mass $m_1 = 1.04m_0$, $m_2 = 0.58m_0$. Equation (5) for κ_D does not apply to low density. At very low density we know that screening is accomplished by binding an electron in a 1s state which gives a screening length $a_0^{\mathrm{BE}}/2$, comparing exponential tails. (a_0^{BE} is the Bohr radius as determined from the binding energy.) We take crude account of this fact by using either κ_D from Eq. (5) or $2/a_0^{\mathrm{BE}}$, whichever is larger. We find $\kappa_{D1} = 1.5 \times 10^7$ cm^{-1}, $\kappa_{D2} = 1.1 \times 10^7$ cm^{-1}. κ_{D1} was found from Eq. (5) while $\kappa_{D2} = 2/a_0^{\mathrm{BE}}$, although κ_{D2} is only 10% larger than Eq. (5) would predict. The appropriate a_0^{BE} was determined by fitting the simple hydrogenic formula to the experimental binding energy. Note that this a_0^{BE} used in estimating κ_D is not the same as the Bohr radius, a_0^*, defined in Eq. (5). The latter requires the use of a density-of-states mass. The length $w_i^{\frac{1}{3}}$ in Eq. (73) is taken equal to κ_{Di}^{-1}.

Using the above values of κ_D in Eq. (47) we compute $\eta_1 = 0.077$ eV, $\eta_2 = 0.063$ eV. The constants a,b,c then have the values $a_1 = a_2 = 1.7$, $b_1 = 0.46$, $b_2 = 0.36$, $c_1 = 1.6$, $c_2 = 1.3$. The Fermi levels are $\zeta_1 = 0.041$ eV, $\zeta_2 = 0.051$ eV. The correction to the Fermi level due to the band tails is negligible.

In Fig. 4 we show the theoretical curve for the I-V characteristic using the band tails given by Eq. (47). Also shown for comparison are the characteristic for the perfect crystal (no tails), the characteristic with tails half as large as given by Eq. (47), and the experimental curve of Logan and Chynoweth.[9] The general agreement between theory and experiment appears satisfactory in view of the roughness of the theoretical approximations. The normalization of the experimental curve is arbitrary but the relative normalization of the three theoretical curves is meaningful. For the same tunneling exponent, λ_0, more current flows when "tails" are present even at very small biases because $E_\perp$ can be larger than the perfect crystal limit, ζ. Since $\bar{E}_1 \sim \zeta \sim \eta$, the effect is significant.

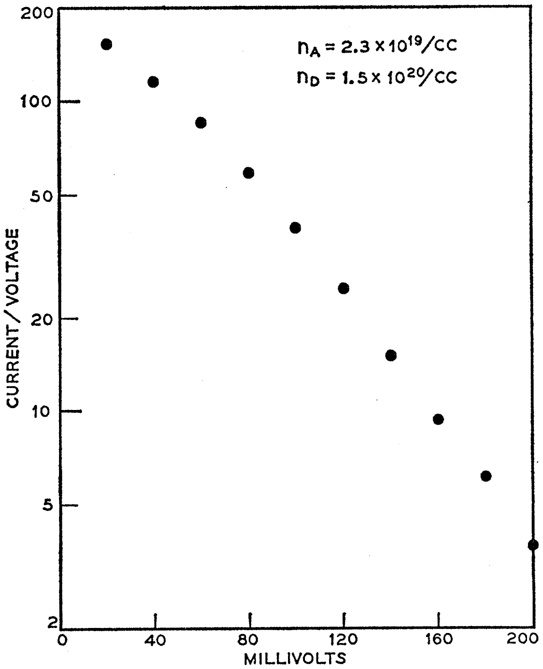

FIG. 6. Theoretical characteristic of Fig. 5(c) plotted as $\log(j/V)$ versus V.

Experiment appears to favor the curves for which the tails have been computed by Eq. (47) rather than those half as large. This result was not expected since we have argued that a proper treatment of the kinetic energy of localization, neglected in deriving Eq. (47), would have the effect of averaging over the potential variations and, hence, narrowing the tails. However, so many approximations have been made in arriving at the experimental results that no strong conclusions should be based on this point.

In Fig. 5 we show the theoretical curves as a function of donor concentration, n_D. The peak voltages in order of increasing concentration are 36, 42, and 56 mV as compared to 33, 36, and 52 mV as given by Logan and Chynoweth. Again, agreement is as good as we have any right to expect.

Because of the many factors entering the theoretical analysis, one would hardly expect the results to display any simple analytic form such as the empirical relationship $j \sim Ve^{\beta V}$ used by Logan and Chynoweth.[9] Nevertheless, Fig. 6 shows that this law is not too badly obeyed, especially for $V > 60$ mV. A noticeable deviation occurs at lower voltages.

ACKNOWLEDGMENT

The authors thanks A. G. Chynoweth for useful discussions.

APPENDIX: TEST OF STATIONARY PHASE METHOD

We test the method of stationary phase used in Sec. IV by applying it to the calculation of the potential distribution function for randomly spaced square wells.

$$\begin{aligned}\mathcal{V}&=v_0, \quad r<r_0\\ &=0, \quad r>r_0.\end{aligned} \tag{A1}$$

The exact solution is easily found to be

$$\begin{aligned}F(\mathcal{V})&=\sum_{m=0}^{\infty}\delta(\mathcal{V}-mv_0)\frac{1}{m!}(nw_0)^m e^{-nw_0},\\ w_0&=4\pi r_0^3/3,\end{aligned} \tag{A2}$$

where we have used Eq. (10), the probability of finding exactly m atoms within the interaction volume w_0 about the origin. n is the average density.

The equations analogous to Eqs. (37) through (39) become

$$\varphi=i\alpha\mathcal{V}+nw_0(e^{-i\alpha v_0}-1), \tag{A3}$$

$$\frac{d\varphi}{d\alpha}=i\mathcal{V}-inv_0w_0e^{-i\alpha v_0}, \tag{A4}$$

$$\frac{d^2\varphi}{d\alpha^2}=-nv_0^2w_0e^{-i\alpha v_0}. \tag{A5}$$

The stationary phase points are

$$-i\alpha_s v_0=\ln(\mathcal{V}/nv_0w_0)+2\pi is, \tag{A6}$$

$$\varphi_s=(\mathcal{V}/v_0)\{1-2\pi is-\ln(\mathcal{V}/nv_0w_0)\}-nw_0, \tag{A7}$$

$$\varphi_s''=-v_0\mathcal{V}. \tag{A8}$$

The distribution function is given by Eq. (40).

$$\begin{aligned}F(\mathcal{V})=\Big[\sum_{S=-\infty}^{\infty}\exp(-2\pi is\mathcal{V}/v_0)\Big]&\frac{1}{(2\pi v_0\mathcal{V})^{1/2}}\\ &\times\left(\frac{nv_0w_0}{\mathcal{V}}\right)^z\exp(-nw_0+\mathcal{V}/v_0),\end{aligned} \tag{A9}$$

$$z\equiv\mathcal{V}/v_0.$$

The sum over s is easily evaluated:

$$\sum_{s=-S}^{+S}e^{is\varphi}=\frac{\sin(S+\frac{1}{2})\varphi}{\sin\frac{1}{2}\varphi}, \tag{A10}$$

$$\lim_{S\to\infty}\sum e^{is\varphi}=2\pi\sum_{m=-\infty}^{\infty}\delta(\varphi-2\pi m). \tag{A11}$$

Using (A11), we find for (A9)

$$\begin{aligned}F(\mathcal{V})=\sum_{m=-\infty}^{\infty}\delta(\mathcal{V}-mv_0)&\frac{1}{(2\pi\mathcal{V}/v_0)^{1/2}}\\ &\times\left(\frac{nv_0w_0}{\mathcal{V}}\right)^z\exp(-nw_0+\mathcal{V}/v_0).\end{aligned} \tag{A12}$$

Equation (A12) agrees with (A2) upon substituting Stirling's approximation for $m!$ and discarding the spurious solutions with m negative. The solution $s=0$ is the only point of stationary phase which could be found by expanding the exponential in (A3) as was done in Sec. IV. Keeping only $s=0$ in Eq. (A9), the result is the same as (A2) if we average the δ function peak over the interval v_0 between peaks. We have been unable to determine what importance other points of stationary phase, if they exist, might have in the problem of Sec. IV. For $n\sim 1$, $F(\mathcal{V})$ could be evaluated numerically, but in view of the limitations on the whole approach imposed by the treatment of the kinetic energy [see Eq. (25)] it does not seem worthwhile.