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Broadening of Impurity Bands in Heavily Doped Semiconductors

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The shapes of deep-lying bands of impurity states broadened by fluctuations in the local Coulomb potential are calculated for the case of randomly distributed ions in a semiconductor and are shown to determine the shapes of the spectral lines emitted by electrons or holes captured in these bands. The distribution function for the local potential is described in terms of its Laplace transform, and expressions for its first few moments, $\bar{E}, \langle (E-\bar{E})^2\rangle_{\text{av}}$, etc., are calculated for screened Coulomb potentials. An approximate form is given for this function and is shown to be reasonably accurate for materials having a high degree of compensation or a large screening length. From the results of this analysis it is shown that the shapes of impurity emission lines can be used to aid in the identification of the nature of the states and transitions involved. In particular, the width of a line is determined principally by the product of the ion density and the screening length in the luminescent region, while the sense of its skewness depends on the signs of the domination and of the carrier which is captured. Numerical examples are given for GaAs diodes containing approximately 10^{18} ions/cm^3.

1. INTRODUCTION

The importance of fluctuations in local potential in perturbing the energies of band states of impure semiconductors has been discussed by Kane[1] and by Bonch-Bruevich.[2] The same fluctuations convert the well-defined energies of deep trapping centers into broad bands of states and contribute to the breadth of the low-energy emission peaks seen in luminescence[3,4] and absorption[5] in material containing such centers. This related problem has not, to our knowledge, been treated quantitatively, although the analysis by Hopfield *et al.*[6] of their pair spectra is based on similar physical principles.

In Sec. 2 of this paper we calculate the potential fluctuations produced by randomly distributed ions and determine the shape of the resulting energy bands. Our approach makes use of the generating function of the energy-density function $P(E)$ from which the moments $\bar{E}$, $\langle (E-\bar{E})^2\rangle_{\text{av}}$, etc., of the band of states are easily obtained. In Sec. 3 we use the fact that the generating function is the Laplace transform of the density function to obtain an approximate expression for the density function itself. This approximate function, having a Gaussian form, is the same as that obtained by Kane[1] and applied by him to tunnel-diode characteristics. These results are applied to emission spectra of luminescence in Sec. 4. In Sec. 5 we give numerical examples appropriate for use with GaAs p-n junctions and indicate the validity for these cases of the Gaussian approximation.

2. POTENTIAL FLUCTUATIONS

The electrostatic potential at a given point in an impure crystal differs from that at a corresponding point in a pure crystal by the total Coulomb potential produced at the point by all the ions in the crystal. (We shall neglect potentials produced by local strains as being of secondary importance.) Hence the local potential at a point depends upon the configuration of ions around that point and fluctuates throughout the crystal about its mean value. The probability $P(E)dE$, of finding the local electronic potential energy within a range dE about E is the sum of the probabilities of all ionic configurations which generate a potential energy in that range.

To obtain explicit expressions for these probability-density functions we assume that ions of one type are distributed randomly throughout the crystal with an average density, N, per unit volume or probability, ρ, per site: $\rho = N/N_s$, where N_s is the density of available ionic sites in the crystal. Thus, in a given region denoted by the index, i, containing g_i ionic sites, the probability of finding exactly n_i ions is[7]

$$P_i(n_i)=\rho^{n_i}(1-\rho)^{g_i-n_i}\binom{g_i}{n_i}, \tag{1}$$

where $\binom{g_i}{n_i}$ is the binomial coefficient expressing the number of ways in which g_i sites may be occupied by exactly n_i ions. This probability $P_i(n_i)$ may be seen to be the coefficient of s^{n_i} in the expansion of its generating function[7]

$$F_i(s)=(\rho s+q)^{g_i}=\sum_{n_i} P_i(n_i)s^{n_i}, \tag{2}$$

where $q=1-\rho$. We note that the identity $F_i(1)=1$ assures us that the sum of all $P_i(n_i)$ is unity. The use of such generating functions provides a powerful tool

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[1] E. O. Kane, Phys. Rev. **131**, 79 (1963).

[2] V. L. Bonch-Bruevich, Fiz. Tverd. Tela **4**, 2660 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1953 (1963)].

[3] M. I. Nathan, G. Burns, S. E. Blum, and J. C. Marinace, Phys. Rev. **132**, 1482 (1963).

[4] T. N. Morgan, M. Pilkuhn, and H. Rupprecht, Phys. Rev. **138**, A1551 (1965).

[5] W. J. Turner (to be published).

[6] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters **10**, 162 (1963).

[7] See, for example, W. Feller, *An Introduction to Probability Theory and its Applications* (John Wiley & Sons, Inc., New York, 1957), 2nd ed., Vol. I, especially Chap. VI, VII (Table I), and XI.

for manipulating the related probability functions. In particular, in combining two regions i and j, the generating function for the combined probabilities, $P_{i+j}(n)$, is the product of the two functions $F_i(s)$ and $F_j(s)$,

$$F_{i+j}(s)=F_i(s)F_j(s)\,, \tag{3}$$

and the procedure may be extended to any number of regions. Thus the problem of forming convolutions is greatly simplified. Although a generating function may not provide an explicit form for the probability function, it does provide easy access to its moments. The following expressions for the moments can be written immediately from (2):

$$\begin{aligned}\bar{n}&=(d/ds)F(s), \quad s=1\\ \langle n^2\rangle_{\text{av}}&=(d/ds)[s(d/ds)F(s)], \quad s=1\\ \langle n^m\rangle_{\text{av}}&=[s(d/ds)]^m F(s), \quad s=1.\end{aligned} \tag{4}$$

These functions are easily modified to describe the probability of finding a particular energy. If each ion (assumed to have a unit positive charge) in the region i contributes to the potential energy of an electron at the point in question an energy $-v_i$ (independent of the positions of all other ions), the total energy contributed by n_i ions is $E_i=-n_iv_i$, and the desired generating function is obtained from (2) by replacing s by s^{-v_i}. Thus

$$G_i(s)=(\rho s^{-v_i}+q)^{g_i}=\sum_{n_i} P_i(n_i)s^{-n_iv_i}=\sum_{E} P(E)s^E\,, \tag{5}$$

where the last sum contains terms for only those energies which can result from one or more arrangements of the ions on the available sites.

With this formalism we can now write down the complete generating function for the energy probability density at a point in the crystal (chosen as the origin of our coordinate system) and can evaluate its moments. If we choose small regions so that the v_i may be considered constant in each, then each configuration of ions contributes an energy $E=-\sum_i n_iv_i$ and the desired generating function is

$$G(s)=\prod_i(\rho s^{-v_i}+q)^{g_i}=\exp[\sum_i g_i\ln(\rho s^{-v_i}+q)]\,, \tag{6}$$

where the sum extends over the entire crystal. As the potential energy v_i at the origin is a function only of r, the distance of the ion from the origin, the regions can be chosen to be spherical shells of thickness dr with $v_i=v(r)$ and $g_i=4\pi N_s r^2dr$, and the sum can be replaced by an integral

$$G(s)=\exp\left[4\pi N_s\int r^2\ln(\rho s^{-v(r)}+1-\rho)dr\right]. \tag{7}$$

Up to this point the treatment has been exact. In (7) we shall make the assumption, which is nearly always justified, that ρ is small compared to 1, and shall neglect terms in ρ^2. In addition we must limit the range of integration to exclude a small sphere near $r=0$ where no sites are located. Thus by letting r range from r_0 to ∞ with r_0 chosen to be about half the lattice constant a_0 we can correctly account for the missing site and at the same time eliminate the divergences associated with the tail of the distribution. In any experiment where structure in the tail is important (as in the pair spectra discussed by Hopfield *et al.*[6]) the discrete nature of the ion sites and their number must be specifically considered.

For small ρ we can expand the logarithm in (7) and neglect terms in $N_s\rho^2=N\rho$ to obtain

$$G(s)=\exp\left[4\pi N\int_{r_0}^{\infty} r^2(s^{-v(r)}-1)dr\right]=\int P(E)s^EdE. \tag{8}$$

The first moment obtained from this function is

$$\bar{E}=G'(1)=-4\pi N\int_{r_0}^{\infty} r^2v(r)dr\,, \tag{9}$$

which will be absorbed in a shift of the origin in the following calculations. The next two moments taken about the mean are

$$\langle(E-\bar{E})^2\rangle_{\text{av}}=\langle E^2\rangle_{\text{av}}-\bar{E}^2=4\pi N\int_{r_0}^{\infty} r^2v^2(r)dr \tag{10}$$

and

$$\begin{aligned}\langle(E-\bar{E})^3\rangle_{\text{av}}&=\langle E^3\rangle_{\text{av}}-3\bar{E}\langle E^2\rangle_{\text{av}}+2\bar{E}^3\\ &=-4\pi N\int_{r_0}^{\infty} r^2v^3(r)dr.\end{aligned} \tag{11}$$

Higher moments are found to be somewhat more complex.

If several species of ions are present, differing in charge Z and density N_z, the potential function of each is multiplied by Z and the integrals are multiplied by N_z and summed over z. Thus the factor N in Eqs. (9), (10), and (11) is replaced by $\sum_z N_zZ$, $\sum_z N_zZ^2$, and $\sum_z N_zZ^3$, respectively, and we find that ions of opposite sign add constructively in the even moments but tend to cancel in the odd moments.

The second and third moments are generally adequate to describe the shape of one of these distributions, as they specify its width and skewness. For screened Coulomb potentials, with screening length, λ, and dielectric constant K, $v(r)=(e^2/Kr)\exp(-r/\lambda)$ and the second moment becomes

$$\begin{aligned}\sigma^2=\langle(E-\bar{E})^2\rangle_{\text{av}}&=(4\pi e^4/K^2)\sum_z N_zZ^2\int_{r_0}^{\infty}\exp(-2r/\lambda)dr\\ &=(2\pi e^4/K^2)\lambda\sum_z N_zZ^2\exp(-2r_0/\lambda)\,.\end{aligned} \tag{12}$$

The third moment is

$$\begin{aligned}\langle (E-\bar{E})^3\rangle_{\rm av} &= -(4\pi e^6/K^3)\sum_z N_z Z^3\int_{r_0}^{\infty}(dr/r)\exp(-3r/\lambda)\\ &= -(4\pi e^6/K^3)\sum_z N_z Z^3[-Ei(-3r_0/\lambda)],\end{aligned} \qquad (13)$$

where the exponential integral[8] is nearly logarithmic in r_0/λ.

The significance of these results and of those of Sec. 3 in understanding deep energy levels in impure solids is that the fluctuations in potential energy occurring between the different sites of deep impurity centers in a crystal produce identical fluctuations in the energies of the highly localized states associated with these centers. If impurity atoms are distributed at random, their electronic energy levels are displaced by an energy E with the probability $P(E)$ discussed above, and the moments given in (12) and (13) are the moments of the resulting bands of states. This conclusion is strictly true only for highly localized (deep) centers but can be used with reservations under less restrictive assumptions.[1]

3. THE PROBABILITY-DENSITY FUNCTION $P(E)$

Equation (8) completely determines the probability-density function $P(E)$, since the generating function is an integral transform of this function. To obtain a more familiar form for this transform we substitute $s=\exp(-t)$ and write the generating function as

$$\phi(t)=\exp\left[4\pi N\int_{r_0}^{\infty} r^2(e^{vt}-1)dr\right] = \int_0^{\infty} P(E)e^{-Et}dE. \qquad (14)$$

Thus $\phi(t)$ is the Laplace transform of the function $P(E)$, and the inverse transform can be written immediately,[9]

$$P(E)=\left(\frac{1}{2\pi i}\right)\int_{\mu-i\infty}^{\mu+i\infty}\phi(t)e^{Et}dt. \qquad (15)$$

The value of this integral is independent of the parameter μ which may be chosen for convenience or set equal to zero [though in certain cases μ must be chosen to avoid singularities in $\phi(t)$]. In our applications of this result it will be convenient to measure E from its mean value $\bar{E}$. We see from (14) that to shift the origin in energy space by $\bar{E}$ we must multiply $\phi(t)$ by $\exp(\bar{E}t)$. The result of this operation with the value of $\bar{E}$ taken from Eq. (9) is

$$P(E)=\left(\frac{1}{2\pi i}\right) \times\int_{\mu-i\infty}^{\mu+i\infty}\exp\left[4\pi N\int_{r_0}^{\infty} r^2(e^{vt}-1-vt)dr+Et\right]dt. \qquad (16)$$

Equation (16) with $\mu=0$ is the same integral obtained by Kane[1] [his Eq. (36)] from a slightly different though, as we see, physically equivalent model. The cutoff radius r_0 enters here as a natural consequence of the crystal lattice structure and for our purposes can be quite small. Kane was concerned with band states which could not be localized arbitrarily, so that a larger value of r_0 was appropriate. The ions lying near the origin affect only the tail of the distribution ($e^2/Kr_0\approx 0.5$ eV in GaAs), and are unimportant in describing the center of the distribution.

To obtain an approximate expression in closed form for $P(E)$ we shall make use of the expansion of $\ln\phi(t)$ in powers of v and keep only the term in v^2—equivalent to specifying the second moment,[10] Eq. (10). This approximation will be best in compensated materials (as near a graded *p-n* junction) where ions of both signs are present and the third moment (11) is small. In uncompensated materials, though the skewness is lost and the tails are not accurately described, the width can be specified with reasonable accuracy in many cases. Thus, keeping only the first nonvanishing term in the r integrand in (16) and writing the variance as $\langle (E-\bar{E})^2\rangle_{\rm av}=\sigma^2$, we obtain

$$P(E)=\left(\frac{1}{2\pi}\right)\int_{-\infty}^{\infty}\exp[\sigma^2(\mu^2-\tau^2)/2 +E\mu+i(\sigma^2\mu+E)\tau]d\tau, \qquad (17)$$

where the variable of integration has been written $t=\mu+i\tau$. This integral is most easily evaluated if we eliminate the imaginary exponent by choosing $\mu=-E/\sigma^2$ to obtain the result,

$$P(E)=(2\pi)^{-1/2}\sigma^{-1}\exp(-E^2/2\sigma^2). \qquad (18)$$

This is the normal density function (Gaussian) and is the same result obtained by Kane.[1] It is a convenient though frequently inaccurate function for describing the shapes of the bands of impurity states occurring in impure semiconductors. For strongly skewed distributions a more meaningful function of this type can often be constructed if an effective value of σ^2 is chosen giving a better fit of (18) to the true band shape around its maximum $E^2<4\sigma^2$. We describe in the following

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[8] E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, Inc., New York, 1945).

[9] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1962), Vol. II, p. 535 ff. Their presentation also discusses the validity of (15) if $P(E)=0$, $E\leq 0$.

[10] An expansion involving higher moments and Hermite polynomials of argument $(E-\bar{E})/\sigma$ can be used, though to little advantage because of the large size of the higher moments; see H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand, Inc., Princeton, New Jersey, 1943), Sec. 12.3 and reference to the work of F. Zernike.

paragraph a simple method for testing the accuracy of (18) and at the same time estimating an effective value of σ^2.

Integration of (18) over energy from $-\infty$ to E converts it into the normal distribution function[7] $\Phi(E/\sigma)$, which varies monotonically from zero to one as E increases from $-\infty$ to $+\infty$. As $\Phi(2.3)=0.99$, all but 1% of the states in the band described by (18) lie below $E=2.3\sigma$, and the value of $\langle E^2\rangle_{\text{av}}$ computed from this range is

$$\int_{-\infty}^{2.3\sigma} E^2P(E)dE \Big/ \int_{-\infty}^{2.3\sigma} P(E)dE=0.93\sigma^2.$$

Thus if the contribution to the value of σ^2 from the energy range $E>2.3\sigma$ is significantly greater than the 7% expected for a Gaussian, the function (18) gives a poor description of the true band shape. In this case an effective value of σ^2 for use in (18) can be computed from the true distribution if only energies below approximately this limit are used (with the result increased by 7% in compensation). To achieve this, approximately, we increase the value of r_0 in (12) to exclude from the integral all lattice sites which, if occupied by an ion, would contribute an energy of more than about 2.3σ. (The probability of finding two ions in this range of r is normally very small.) Thus we choose for σ^2 in (18) the value

$$\sigma_{\text{eff}}^2=1.07(2\pi e^4/K^2)\lambda \sum_z N_z Z^2 \exp(-2R_z/\lambda), \qquad (19)$$

with

$$e^2Z/KR_z \exp(-R_z/\lambda)=2.3\sigma_{\text{eff}}. \qquad (20)$$

This correction is only approximate because of the energy contributions from outside the region, but it generally gives a more realistic estimate of the band width than does (12), and also provides a test of the accuracy of the symmetrized function (18). In applications where the skewness of the band or the shape of the low- or high-energy tail is important, however, we shall make use of the third or higher moments discussed above in Sec. 2. It is significant to note that the true density function (16) normally decreases less rapidly in the tail (on the side which corresponds to small r) than does the approximate function (18).

We now proceed to apply this information to an analysis of emission spectra from deep centers in heavily doped semiconductors.

4. THE SHAPE OF EMISSION LINES

Using the expressions developed in the preceding sections for the shape of the bands of impurity states, we can draw some conclusions about the shape of the optical emission lines produced when free electrons (or holes) are captured on impurities. If the electrons are captured from a narrow range of states, say near the Fermi level, at a rate which is uniform over the entire band, the emission line will have the same shape as the impurity band. In reality the carriers originate in a range of states which also depend upon the local potential, and the capture rate may not be uniform over the band. For these reasons we cannot unambiguously determine the line shapes without undertaking an extensive analysis of the nature of the band states and capture processes in these impure materials. Rather than attempt such an analysis we shall be content with results of a qualitative or semiquantitative nature.

We shall base our discussion on the assertion that, except in certain special cases which we consider below, the spectral emission lines have nearly the same shape as the impurity bands and provide a means of measuring the approximate width and skewness of the latter. Support for this assertion comes from the ease with which electrons and light holes near the Fermi level in the common semiconductors can tunnel through the potential barriers raised by the local energy fluctuations, and from the fact that even an exponentially varying capture rate has little effect on the shape of a nearly Gaussian emission line. This latter result is a consequence of the fact that the product of a Gaussian function and an exponential is a displaced Gaussian having the same width,

$$\begin{aligned}&\exp(\gamma x)\exp(-x^2/2\sigma^2)\\ &\qquad=\exp(\gamma^2\sigma^2/2)\exp[-(x-\gamma\sigma^2)^2/2\sigma^2]. \qquad (21)\end{aligned}$$

As a final test of this assertion we can compare the observed and computed line shapes from copper-doped GaAs.[11]

The results of Secs. 2 and 3 can now be used to predict or interpret the low-temperature emission spectra from radiative capture on impurity centers. (The additional modifications in shape which occur at high temperatures will not be considered in this paper.) In particular, a wide line is expected from a region having a high charge density and a large screening length, while a region in which these quantities are small will emit a narrow line. The sense of the skewness of a line depends not only on the third moment, (13), but also on the sign of the carrier which is captured. Thus in n-type material where the bands are skewed toward low electron energies ($\sum_z N_z Z^3>0$), holes when captured emit lines skewed toward low energies, while electrons

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[11] In Ref. 4 it is shown that capture of an electron on a singly charged copper acceptor occurs principally on the n side of the junction and produces an emission line near 1.0 eV. From our analysis we expect this center to produce a band of states having a width at half-maximum of about 70 meV and causing emission of a line skewed toward high photon energies. The observed line, number 4 at 1.06 eV, has a width of 75 meV and a tail extending toward high energy as predicted. Similarly, capture of an electron on a neutral copper acceptor occurs principally within the space-charge region and produces a broad, nearly symmetrical line. The width of this line is estimated to be 170 meV while the observed line, number 3 at 1.29 eV, has a width of 148 meV and is slightly skewed toward low energy. Thus, the assertion that the energy-band shapes determine the emission-line shapes appears justified.

emit lines skewed toward high energies. The opposite is true in *p*-type material.

In the interpretation of electroluminescent spectra from *p-n* junctions, these differences can become quite useful in determining the nature of the transitions and the location in the device of the source of the radiation. The width of emission lines from a diode can vary appreciably according to the locus of the source of the radiation. In the *n*- and *p*-type material near the junction the screening lengths differ according to the square roots of the effective masses—in GaAs, $\lambda_n \approx 3\lambda_p$ for the same carrier density—while in the junction region the effective-screening length λ^* is increased by approximately half the junction width,[12]

$$\lambda^* \approx 2[\lambda_n\lambda_p/(\lambda_n+\lambda_p)]+[(\lambda_n^2+\lambda_p^2)/(\lambda_n+\lambda_p)^2]w. \quad (22)$$

Thus the width alone may be sufficient to locate the source, so that skewed lines may be identified with the capture of electrons or holes without ambiguity.

Modifications in both skewness and linewidth can reresult if the transition involves a partially occupied band of states. In this case $P(E)$ is multiplied by the Fermi factor, and a simple Gaussian band gives a line shape (assuming a unity degeneracy ratio) of approximately

$$P(E)f(E)=(2\pi)^{-1/2}\sigma^{-1} \times \exp(-E^2/2\sigma^2)\bigg/\left[1+\exp\left(\frac{E-E_f}{kT}\right)\right] \quad (23a)$$

for capture of holes and

$$P(E)[1-f(E)]=(2\pi)^{-1/2}\sigma^{-1} \times \exp(-E^2/2\sigma^2)\bigg/\left[1+\exp\left(\frac{E_f-E}{kT}\right)\right] \quad (23b)$$

for capture of electrons. The position of the Fermi level E_f at low temperature depends only on σ and the fraction n/N_i of states occupied. This fraction equals the integral of $P(E)$ over energy from $-\infty$ to E_f,[13]

$$n/N_i=\tfrac{1}{2}[1+\mathrm{erf}(E_f/\sqrt{2}\sigma)]. \quad (24)$$

The temperature dependence of E_f is more complex, though some information about the temperature dependence of the position of the emission peak from a partially filled band can be found by differentiation of (23).

Proper consideration of this dependence of the Fermi energy on the value of n (and T) for a partially filled band can be quite important for the correct interpretation of Hall data in heavily doped materials, as a shift of the Fermi level toward the band edge can permit thermally activated carrier densities to persist to quite low temperatures.[4] At low temperature, where E_f is given by (24), the activation energy deduced from Hall or resistivity measurements of the free-carrier density is measured from the energy E_f rather than from the center of the band. This fact accounts for the range of activation energies frequently observed for a single impurity species in impure materials,[4] since the measured activation energy depends upon the value of σ as well as upon the amount of compensation in the sample. A similar change (reduction) in the activation energy is produced by tailing of the band edges. These band tails can also produce changes in emission line shape, although the decreased tunneling probability expected for states deep in the tail tends to reduce their importance. Though these band tail effects cannot be ignored, their calculation is beyond the scope of this paper.[14]

A further modification of the line shape produced by partial filling of a band results from the screening action of the trapped charges, and will be discussed briefly.[15] For convenience, we consider the specific case of electrons released from shallow donors and trapped on deep acceptor states. If the density of acceptors is higher than the density of donors, only the low-energy states in the acceptor band will be filled. Thus the acceptor centers lying near the positive donor ions are preferentially occupied, and the trapped electrons and ionized donors effectively screen each others' potentials. The screening length expected from a degenerate distribution of charges depends upon the density of states at the Fermi level, $n'(E_f)$:

$$\lambda^{-2}=(4\pi e^2/K)n'(E_f). \quad (25)$$

If the charges cannot move freely throughout the volume of the crystal, their effective screening is reduced by their inability to get close to the ions. An estimate of their effective-screening length λ^* can be made from Debye-Hückel electrolyte theory,[16] where the screening of mobile ions depends upon the distance of closest approach a of two ions

$$\lambda^*=\lambda+a. \quad (26)$$

In the present problem the distance a is not uniquely defined but can be taken with reasonable accuracy to be the mean distance between ions

$$a=(3/4\pi N_T)^{1/3}, \quad (27)$$

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[12] This effective screening length is chosen to give the same value of σ^2 in (12) as that found at the midplane of the junction. It has been obtained from the solution of the appropriate boundary-value problem (for a charge located on the midplane of the junction) by integration of $V^2(r)$ over all space. We give the first two terms in the expansion of the integral in powers of w/λ, valid for $w/\lambda \ll 1$. If $w/\lambda \gg 1$, $\lambda^* \approx w/2$. T. N. Morgan (to be published).

[13] H. B. Dwight, *Tables of Integrals and Other Mathematical Data* (The Macmillan Company, New York, 1947), p. 129.

[14] A manuscript describing an analysis of the band tails using Laplace transforms is in preparation.

[15] A similar screening problem in the high-temperature (nondegenerate) limit has been discussed by W. W. Harvey, Phys. Rev. **123**, 1666 (1961).

[16] For a summary of Debye-Hückel theory see S. Glasstone, *Thermodynamics for Chemists* (D. Van Nostrand Inc., Princeton, New Jersey, 1947), Chap. XVII, especially Eq. (40.3).

TABLE I. Moments computed for GaAs crystals containign various concentrations of shallow donors N_D and shallow acceptors N_A. The entries in the last column are cutoff radii (20) (in units of the screening length) for the ions; see text.

N_D (10^{18} cm^{-3})	N_A (10^{18} cm^{-3})	$\bar{E}$ (meV)	σ (meV)	$\langle(E-\bar{E})^3\rangle_{\text{av}}{}^{1/3}$ (meV)	σ_{eff} (meV)	$R_{\pm 1}/\lambda$
1.0	0	−33.4	19.0	−30.0	13.1	0.49
0	1.0	3.3	9.6	22	0.8	2.7
1.1	1.0	−7.2	29.7	−14.3	25.3	0.27
1.0	1.1	0.7	15.4	10.8	4.2	1.50
1.0	1.0	0	46.8	0	47.2	0.07

where N_T is the total density of centers, donors plus acceptors. With this assumption the effective-screening length becomes

$$\lambda^* = \{K/[4\pi e^2 n'(E_f)]\}^{1/2} + (3/4\pi N_T)^{1/3}. \tag{28}$$

As $n'(E_f)$ depends on σ (both explicitly and through E_f)

$$n'(E_f) = (N/(2\pi)^{1/2}\sigma)\exp(-E_f{}^2/2\sigma^2), \tag{29}$$

a simultaneous solution of (28) and (12) is needed to determine σ. If free carriers are also present, their effect can be added in the usual way,

$$1/\lambda^2 = 1/\lambda_1{}^2 + 1/\lambda_2{}^2.$$

5. NUMERICAL EXAMPLES FOR GaAs

To show the importance of the effects discussed above we choose GaAs as a typical and popular semiconductor and calculate the moments and band shapes for material doped in the $10^{18}/\text{cm}^3$ range. We use the parameters $K = 12.5$, $m_n = 0.072\, m$, $m_p = 0.68\, m$, and $r_0 = 2.5\times 10^{-8}$ cm. Hence for degenerate carriers $\lambda_n = 4.8\times 10^{-4} n^{-1/6}$ cm and $\lambda_p = 1.54\times 10^{-4} p^{-1/6}$ cm.

In uncompensated n-type material ($Z=1$), the first three moments, (9), (12), and (13), are

$$\begin{aligned}\bar{E} &= -(4\pi n e^2\lambda^2/K)(1+r_0/\lambda)\exp(-r_0/\lambda) \\ &= -3.34\times 10^{-11} n^{2/3}\ \text{meV}\end{aligned} \tag{30a}$$

as $(r_0/\lambda)^2 \ll 1$,

$$\begin{aligned}\sigma^2 &= 8.34\times 10^{-10}\lambda n \exp(-10^{-4} n^{1/6}) \\ &= 4.00\times 10^{-13} n^{5/6}\exp(-10^{-4} n^{1/6})\,(\text{meV})^2,\end{aligned} \tag{30b}$$

and

$$\begin{aligned}\langle(E-\bar{E})^3\rangle_{\text{av}} &= -1.92\times 10^{-14} n \\ &\quad\times[-\text{Ei}(-1.56\times 10^{-4} n^{1/6})]\,(\text{meV})^3.\end{aligned} \tag{30c}$$

The values of these expressions for $n = 10^{18}$ cm^{-3} are listed in the first horizontal line of Table I, as are the values of σ_{eff} and the ratio R_{+1}/λ given by (19) and (20). Comparison of the three moments shows that the distribution is moderately asymmetric. The approximate agreement between σ and σ_{eff} confirms this and indicates that the symmetric function (18) represents the probability in the middle-energy region fairly well.

For uncompensated p-type material with $p = 10^{18}$ cm^{-3} the calculated quantities are given in the second line of the table. The small value of λ_p causes the distribution to be highly asymmetric, as a relatively small number of nearby ions makes a large contribution to the fluctuations. This is reflected in the unreasonably small value of the effective standard deviation σ_{eff} and in the large value of the cut-off radius $R_{-1} = 2.7\lambda$. It indicates that the symmetrized distribution (18) is a poor approximation for this case.

In compensated n and p material, listed in the third and fourth lines of the table, the cancellation of the effects of the positive and negative ions in the odd moments and the larger values of σ produce more symmetric distributions which are better fitted by (18). In spite of this, the value of σ_{eff} calculated for the p-type material is a factor of 4 below the true value of σ, and the symmetric approximation gives only a poor indication of the true shape of the bands.

Finally, in the space-charge region of a p-n junction of width $w = 1.8\times 10^{-6}$ cm, the complete cancellation in the odd moments (for singly charged ions) gives an essentially symmetric distribution (neglecting asymmetries in screening on the n and p sides) which the Gaussian approximation describes quite accurately. The values of σ and σ_{eff} calculated for this case, with screening provided by $10^{17}/\text{cm}^3$ electrons and holes at the edges of the space-charge region, are entered in the final line of Table I. ($\lambda^* = 1.36\times 10^{-6}$ cm.) The effective standard deviation is seen to be little different from the true value, and the value calculated from (14) for the fourth moment exceeds that of a Gaussian $3\sigma^4$ by only 2.5%.

These examples serve to illustrate the experimental circumstances under which various approximations may be used and to point out their limitations. Extensions of the results to other densities and materials are easily made.