⟨000⟩ minima band and n_1 the number in the ⟨111⟩ band, then the total number of electrons is given by $n = n_0 + n_1$. Figure 5 shows the variation of m^* with n from Table II. It may be seen from this figure that m^* increases with the increase in n. One can also correlate the density-of-states effective mass m^* with m_0^* and m_1^* by the following relation:

$$1/m^* = \gamma/m_0^* + (1-\gamma)/m_1^* ,$$

where

$$\gamma = n_0/(n_0+n_1) = n_0/n .$$

Since the values of m_0^* and m_1^* are known from magnetoresistance measurements, it should be possible to calculate the number of electrons in the ⟨111⟩ minima band for a given value of n. Table II gives the values of n_0 and n_1 for different values of n. It may be seen from this table that at low concentrations of the order $1-2\times10^{17}$ cm^{-3} the phonons are scattered by electrons in the ⟨000⟩ band. For large concentrations, n exceeding 1×10^{18} cm^{-3}, the phonons are scattered by electrons in the ⟨111⟩ minima band. For intermediate concentrations, the phonons are scattered by electrons from both the bands, and this is the reason that m^* lies in between the two extreme values 0.05 and 0.5. It may be further concluded that with the low electron concentrations the impurity states merge with the ⟨000⟩ minima band and with further increase in the concentration, they also merge with the ⟨111⟩ minima bands.

It is also concluded that the contribution of electron-phonon scattering to the lattice thermal resistance is maximum at the lowest temperature and a reduction is obtained at temperatures above the conductivity maximum.

It is also observed that electron-phonon scattering is strongly dependent on frequency and the low-frequency phonons are scattered most effectively.

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Nonequilibrium Steady-State Statistics and Associated Effects for Insulators and Semiconductors Containing an Arbitrary Distribution of Traps

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The statistics for an arbitrary distribution of traps under nonequilibrium steady-state conditions is derived, and it is seen to be identical in form to the Shockley-Read expression for a single trapping level. The energy dependence of the statistics has been investigated, and several interesting features have been deduced. It has been found appropriate to describe the occupancy of the traps in terms of two *modulated* Fermi-Dirac functions—one associated with trapped electrons, the other with trapped holes. It has been found possible to categorize the traps (into species) in terms of the ratio of their electron and hole capture cross sections. Detailed discussions are given for the electron and hole fillings of the traps as a function of energy, temperature, and illumination intensity for various trap distributions. The distinctions between shallow traps, recombination centers, and *dead* states are defined and discussed in detail.

I. INTRODUCTION

Shockley-Read[1] statistics have been extremely successful in describing nonequilibrium steady-state processes in semiconductors. The original work was concerned with the recombination processes occurring through a single discrete trapping level. A formal extension of the theory, using the traditional Shockley-Read approach, to more than one distinct trapping level results in equations of extreme algebraic complexity.[2] As a result the problem has rarely been treated beyond this level in a strictly formal manner. This is not unduly restrictive if the theory is to be applied to the technologically important semiconductors such as silicon or germanium. These materials are normally grown to such a high degree of crystalline perfection and purity that the nonequilibrium recombination and generation processes are often controlled by one dominant trapping level.

In the case of crystalline insulators, experimental evidence suggests that the trapping levels are distributed throughout the forbidden band gap.[3–5] In polycrystalline materials one intuitively expects to find a wide variety of trapping levels. As regards amorphous solids, both theory and experiment suggest the existence of localized levels[6] throughout the band gap. These localized levels are an *intrinsic* property of amorphous materials and arise from the lack of long-range order in such materials. Thus one cannot analyze such systems with a theory, the applicability of which is limited to one or two trapping levels.

Rose has attacked the distributed trap problem using a semiquantitative approach (and some remarkable physical intuition) with a good deal of success.[7] However, such an approach is limited in the sense that it is difficult to obtain much quantitative information about the system. Also it can be applied only to simple systems, because of the very complexity of the problem which involves several simultaneous and interacting processes.

In this paper we have tackled the distributed trap problem on strictly formal grounds. The approach is quite general and the results are applicable to an arbitrary distribution of traps and an arbitrary distribution of trap cross sections.

II. PRELIMINARY REMARKS

It is sometimes assumed in the literature that electron and hole traps are distinct physical entities. This is not the case. A trap is amphoteric in the sense that it acts both as an electron trap and as a hole trap, and it is its *state of occupancy* that determines in which capacity it is acting. When the trap is empty, it is ready to receive an electron, and thus it is operating as an electron trap. When the trap contains an electron, it is ready to receive a hole, and hence is a hole trap. (We are assuming that the trap is monovalent.)

It is convenient to assume that the traps existing below the equilibrium Fermi level are neutral when filled with an electron and that the traps positioned above the equilibrium Fermi level are neutral when empty. (This is the condition we have assumed here for convenience, although it is not necessarily the case.) Thus a trap positioned above the equilibrium Fermi level is neutral when acting as an electron trap and negatively charged when acting as a hole trap. On the other hand a trap positioned below the equilibrium Fermi level is neutral when acting as a hole trap and positively charged when acting as an electron trap.

At first thought, it would seem that a positively charged electron trap would have a greater propensity for capturing an electron than a neutral electron trap. This is not necessarily the case but is probably so. However, it should be noted that the efficacy of an electron trap is determined solely by its capture *cross section* for electrons and not by its state of charging, since the cross section of an electron trap implicitly includes its state of charging. Thus, a charged and neutral electron trap having the same cross section will capture electrons at exactly the same rate. Similar remarks pertain to neutral and negatively charged hole traps. In the following discussions, then, we will not be concerned with the state of charging of the traps but rather its cross section for holes and electrons.

III. THEORY

A. Emission and Capture Processes

According to Shockley-Read statistics[1] the four processes which determine the trap occupancy of a discrete trapping level are as indicated in the Fig. 1. Process a is the capture of electrons from the conduction band by the trap; its rate is

$$r_a = v\sigma_n n N_t (1-f) \quad , \tag{1}$$

where n is the free-electron density in the conduction band, v is the thermal velocity of the electrons, σ_n is the capture cross section of the trap for electrons, N_t is the trap density per unit volume, and f is the probability of occupation of a given trap level. Process b is the rate of emission of electrons from the trap; its rate is

$$r_b = e_n N_t f \quad , \tag{2}$$

where e_n is the emission probability from the trap for electrons. Process c is the capture of holes from the valence band; its rate is

$$r_c = v\sigma_p p N_t f \quad , \tag{3}$$

where p is the free-hole density in the valence band and σ_p is the capture cross section for holes. Process d is the rate of emission of holes to the valence band; its rate is

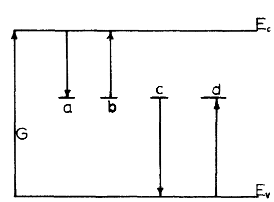

FIG. 1. Transitions taking place under nonequilibrium conditions (Ref. 1).

$$r_d = e_p N_t (1 - f) \quad , \qquad (4)$$

where e_p is the probability of hole emission from the trap.

The emission probabilities e_n, e_p are related to σ_n and σ_p, respectively, from the fact that in thermal equilibrium

$$r_a = r_b \ , \quad r_c = r_d \quad , \qquad (5)$$

and[8]

$$f = \frac{1}{1 + \exp[(E_t - E_{F0})/kT]} \ , \qquad (6)$$

where E_{F0} is the equilibrium Fermi level. This yields

$$e_n = v\sigma_n N_c \, e^{(E_t - E_c)/kT} \quad , \qquad (7)$$

$$e_p = v\sigma_p N_v \, e^{(E_v - E_t)/kT} \quad . \qquad (8)$$

B. The Distribution Function

Consider now the case of a semiconductor or insulator having an arbitrary distribution of traps $N(E)$ per unit volume per unit energy throughout the energy gap, when the solid is uniformly illuminated resulting in a constant generation rate per unit volume G of electron-hole pairs. The statistics of occupancy for the traps may be derived from two different points of view. The first of these is to consider the rate equations for the conduction and valence bands which is used in the Shockley-Read approach. The second is to consider the rate equation for a particular trapping center. Consider the first approach. In nonequilibrium steady state the rate at which electrons enter the conduction band equals the rate at which electrons leave the conduction band; that is,

$$\frac{dn}{dt} = G - \int_{E_v}^{E_c} \bar{n} N(E)[1 - f(E)]\,dE + \int_{E_v}^{E_c} e_n N(E) f(E)\,dE = 0 \quad . \qquad (9)$$

Similarly, the rate at which holes leave the valence band equals the rate at which holes enter the valence band which is

$$\frac{dp}{dt} = G - \int_{E_v}^{E_c} \bar{p} N(E) f(E)\,dE + \int_{E_v}^{E_c} e_p N(E)(1 - f(E)\,dE = 0 \quad , \qquad (10)$$

where E_c is the energy of the bottom of the conduction band, E_v is the energy of the top of the valence band, $\bar{n} = v\sigma_n n$, and $\bar{p} = v\sigma_p p$. From (9) and (10) we have

$$\int_{E_v}^{E_c} N(E)\{-\bar{n}[1 - f(E)] + e_n f(E) + \bar{p} f(E) - e_p[1 - f(E)]\}\,dE = 0 \quad . \qquad (11)$$

Because (11) is valid for an *arbitrary* distribution of traps $N(E)$, the quantity in braces in the integrand can be equated to zero:

$$e_n f(E) - \bar{n}(1 - f(E)) - \bar{p} f(E) + e_p(1 - f(E)) = 0 \quad . \qquad (12)$$

Thus the probability of occupation $f(E)$ of a trap level at *any* energy E is given by

$$f(E) = \frac{\bar{n} + e_p}{e_n + \bar{n} + \bar{p} + e_p} \quad , \qquad (13)$$

which is just the statistic originally derived by Shockley and Read for a single-trap level. However, as we have shown, (13) is a quite *general* statement and is *independent* of the energy distribution of the traps.

Consider now, the rate equation for a particular trap. In the nonequilibrium *steady-state* condition, the occupancy of any trap is constant and thus the four processes which fill and empty the trap are in balance. Therefore,

$$\bar{n} N(E)[1 - f(E)] - e_n N(E)[1 - f(E)] - \bar{p} N(E) f(E) + e_p N(E)[1 - f(E)] = 0 \ , \qquad (14)$$

and the probability of occupation $f(E)$ of a trap level of any energy E is given by

$$f(E) = \frac{\bar{n} + e_p}{e_n + \bar{n} + \bar{p} + e_p} \quad , \qquad (15)$$

which agrees with (13) above.

The two approaches discussed above may appear *prima facia* to be no more than just alternative means of deriving the same statistic; however, each approach inherently contains additional information. Equations (9) and (10) apply to the traps taken collectively. They relate the method of stimulation to the trap distribution and the free-carrier concentrations and are essential if the free-carrier densities are required. On the other hand, $f(E)$ as derived via (14) applies to the traps taken individually and shows that the statistic is independent of the means of stimulation. This observation shows that $f(E)$ can be multivalued at a particular energy *without* being irregular. For example, if we have three traps positioned at the same energy having different cross sections, then clearly $f(E)$ will take three different values.

From the foregoing it would appear that, in a distribution of traps, each trap having different trap cross sections for electrons and holes would require its own distribution function. However, consider a group of traps in the distribution for which the ratio R of the cross sections for electrons and holes,

$$R = \sigma_n(E)/\sigma_p(E) \quad ,$$

is a constant. By inspection of (15) it is seen that *all* traps in this group are defined by a unique function $f(E)$. A *species* of traps is defined by that group of traps characterized by a particular value of R. It will be noted that the cross sections $\sigma_n(E)$ and $\sigma_p(E)$ of any trap in a species may be independent of E or may have the same functional dependence on energy since it is sufficient that R be a constant independent of energy to define a species.

At all energies above the intrinsic Fermi level,[9] E_i, e_p in (13) may be neglected in comparison with e_n, $\bar{n}$, and $\bar{p}$ to yield

$$f = \frac{\bar{n}}{e_n + \bar{n} + \bar{p}} \quad , \quad e_p \ll e_n, \bar{n}, \bar{p} \quad . \tag{16}$$

Similarly for all energies below E_i, e_n in (13) may be neglected in comparison with e_p, $\bar{n}$ and $\bar{p}$ to yield

$$f = \frac{\bar{n} + e_p}{e_p + \bar{n} + \bar{p}} \quad , \quad e_n \ll e_p, \; \bar{n}, \; \bar{p} \quad . \tag{17}$$

C. Insulator Containing a Single Species of Traps

As we are dealing with only one species of traps we are concerned with only a single distribution function.

Figure 2, which illustrates typically the occupancy of traps before and after illumination, contains several interesting features. It will be noted that above the equilibrium Fermi level[10] E_{F0} the occupation probability has increased markedly. Below E_{F0} the occupation probability has considerably decreased.[11]

a. Conditions above E_{F0}. An important feature of (16) for the case in hand is that it has a modulated Fermi-Dirac form about an energy E_{Ft}^n defined by

$$\nu \sigma_n N_c \exp[(E_c - E_{Ft}^n)] = \bar{n} + \bar{p} \ . \tag{18}$$

This is readily shown by writing (16) in the following form:

$$f = \frac{\bar{n}}{(\bar{n} + \bar{p})} \left\{ 1 + \frac{1}{[e_n/(\bar{n} + \bar{p})]} \right\} \quad , \tag{19}$$

and substituting (18),

$$f = \frac{\bar{n}}{\bar{n} + \bar{p}} \left\{ \frac{1}{1 + \exp[(E_t - E_{Ft}^n)/kT]} \right\} \ . \tag{20}$$

The quantity in the braces will be recognized as the Fermi-Dirac function about an energy E_{Ft}^n; the modulating factor $\bar{n}(\bar{n} + \bar{p})^{-1}$ is a constant for a given light intensity.

As a result of Eq. (20), E_{Ft}^n can be defined as the quasi-Fermi level for trapped electrons. This is because traps with energy greater than E_{Ft}^n are essentially empty; that is, the traps are filled according to a Boltzmann's distribution

$$f = \frac{Rn}{Rn + p} \exp[(E_t - E_{Ft}^n)/kT] \qquad (e_n > \bar{n} + \bar{p}) \tag{21}$$

and below E_{Ft}^n they are substantially occupied to a constant level given by

$$f = \frac{Rn}{Rn + p} \qquad (e_n < \bar{n} + \bar{p}) \ . \tag{22}$$

The quasi-Fermi level E_{Fn} for free electrons in the conduction band is defined by

$$n = N_c \exp[(E_{Fn} - E_c)/kT] \ . \tag{23}$$

By inspection of (18) and (23) it will be apparent that

$$E_{Ft}^n > E_{Fn} \tag{24}$$

at all times under nonequilibrium steady-state conditions. Thus the quasi-Fermi level for trapped electrons is always positioned (energetically) above the quasi-Fermi level for free electrons, as indicated in Fig. 2. The two coincide when the solid is in thermal equilibrium.

The demarcation level for an electron trap E_{dn} has been defined by Rose[5] as that energy level at which an electron in a trap will have equal probabilities of being thermally excited to the conduction band or of recombining with a free hole. From this definition and (2) and (3),

$$\frac{r_b}{r_c} = \frac{\nu \sigma_n N_c \exp[-(E_c - E_{dn})/kT]}{\nu \sigma_p N_v \exp[-(E_{Fp} - E_v)/kT]} = 1 \quad , \tag{25}$$

from which

$$E_{dn} = E_v + (E_c - E_{Fp}) + kT \ln(\sigma_p N_v / \sigma_n N_c) \quad , \tag{26}$$

where E_{Fp} is the quasi-Fermi level for free holes. Thus if an occupied trap lies higher in energy than E_{dn} then the electron will have a greater probability of being emitted to the conduction band than of recombining with a free hole; otherwise, the converse is true. It would appear attractive to use the demarcation energy to distinguish between shallow traps and recombination centers. However, it will be shown that this is not the case, and that the quasi-Fermi level for trapped electrons provides the most appropriate distinction between shallow traps and recombination centers. Nevertheless it is convenient to retain the concept of a demarcation energy for trapped electrons since it defines an *electron dead* state.

By inspection of (18) and (26) it will be seen that

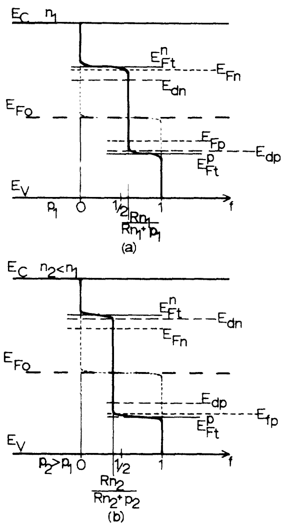

FIG. 2. Two typical occupational functions for an arbitrary distribution of traps.

the demarcation energy is always less than the quasi-Fermi level for trapped electrons. If $\bar{p} > \bar{n}$ then from (23) and (26) the demarcation energy is greater than the quasi-Fermi level for free electrons; otherwise the converse applies.

b. Conditions below E_{F0}. For energies below E_{F0} it is more appropriate to write (17) as

$$1 - f = \bar{p}/(\bar{n} + \bar{p} + e_p) \tag{27}$$

for reasons that will become apparent shortly. Similarly to (16), (27) also has a modulated Fermi-Dirac form with respect to holes about an energy E_{Ft}^{p} defined by

$$v\sigma_p N_v \exp[(E_{Ft}^{p} - E_v)/kT] = \bar{n} + \bar{p} \ . \tag{28}$$

This can be shown by rewriting (27) and substituting (28) to yield

$$1 - f = \frac{\bar{p}}{(\bar{n} + \bar{p})}\left[1 + \exp\left(\frac{E_t - E_{Ft}^{p}}{kT}\right)^{-1}\right] \tag{29}$$

The quantity in the square brackets will be recognized as the Fermi-Dirac function for holes about an energy E_{Ft}^{p}; the modulating term $\bar{p}(\bar{n}+\bar{p})^{-1}$ is a constant for a given light intensity. As a result of (29), E_{Ft}^{p} is now defined as the quasi-Fermi level for trapped holes. This follows from the fact that traps with energies less than E_{Ft}^{p} are essentially full, or in other words the traps are filled with holes according to a Boltzmann's distribution,

$$1 - f = \frac{p}{Rn + p} \exp\left[\frac{(E_{Ft}^{p} - E_t)}{kT}\right] \qquad (e_p > \bar{n} + \bar{p}), \tag{30}$$

and above E_{Ft}^{p} they are substantially filled with holes to a constant level given by

$$1 - f = p/(Rn + p) \qquad (e_p < \bar{n} + \bar{p}) \ . \tag{31}$$

The quasi-Fermi level for free holes in the valence band is defined by

$$p = N_v \exp[(E_v - E_{Fp})/kT] \ . \tag{32}$$

By inspection of (28) and (32) it is apparent that $E_{Ft}^{p} < E_{Fp}$ at all times under nonequilibrium steady-state conditions; thus the quasi-Fermi level for holes is always positioned above the quasi-Fermi level for trapped holes as shown in Fig. 2. Here, also, the two energy levels coincide under steady-state conditions only when thermal equilibrium is attained.

By analogy with E_{dn}, we can define a hole-trap demarcation energy E_{dp} given by

$$E_{dp} = E_c - (E_{Fn} - E_v) + kT\ln(\sigma_n N_c/\sigma_p N_v) \ . \tag{33}$$

Thus if the trap level lies below E_{dp}, then from (1), (4), and (30) the hole will have a greater probability of being emitted to the valence band ($r_d/r_a > 1$). If the trap level lies above E_{dp}, the hole will have a greater probability of recombining with an electron from the conduction band ($r_d/r_a < 1$). Again, the idea of using the hole demarcation energy appears suitable for the separation of shallow hole traps from recombination centers.[3-5] We will show in the discussion[12] that the quasi-Fermi level for trapped holes is a better way of distinguishing between the two. The concept of demarcation energy for hole traps will however prove useful in defining hole *dead states*. E_{dp} is always greater in energy than E_{Ft}^{p}, the quasi-Fermi energy for trapped holes. It is also less than E_{Fp}, the quasi-Fermi level for free holes, if $\bar{n} > \bar{p}$, and greater than E_{Fp} if $\bar{n} < \bar{p}$.

D. Insulator Containing Multiple Species of Traps

In this section we consider a solid in which the arbitrary trap distribution consists of several species S, each different species being characterized by the ratio of the trap cross sections for electrons and holes:

$$\sigma_n(S, E)/\sigma_p(S, E) = R(S) \ .$$

Thus each species may be treated on a separate basis as described in Sec. IIIB.

Above E_{F0} each trap species has a true Fermi-Dirac form about an energy $E_{Ft}^{n}(S)$ defined by

$$v\sigma_n(S, E)N_c \exp\{[E_c - E_{Ft}^{n}(S)]/kT\} = v\sigma_n(S, E)n + v\sigma_p(S, E)p \ , \tag{34}$$

where $\sigma_n(S, E)$ and $\sigma_p(S, E)$ are the electron- and hole-trap cross sections, respectively, for a particular species. The electron occupation function $f(S, E)$ for each species S may be written as

$$f(S, E)=\frac{R(S, E)n}{R(S, E)n+p}\left[1+\exp\frac{E_t-E^n_{Ft}(S)}{kT}\right]^{-1}. \quad (35)$$

Below E_{F0} each trap species has an occupation function f such that $1-f$ has a true Fermi-Dirac form about an energy $E^p_{Ft}(S)$ defined by

$$v\sigma_p(S, E)N_v\exp[(E^p_{Ft}(S)-E_v)/kT] = v\sigma_n(S, E)n+v\sigma_p(S, E)p \quad . \quad (36)$$

The hole occupation function $1-f(S, E)$ for each species S may be written as

$$1-f(S, E)=\frac{p}{R(S, E)n+p}\left[1+\exp\frac{E_t-E^p_{Ft}(S)}{kT}\right]^{-1} \quad (37)$$

The remarks made concerning the occupancy of the traps above and below both the quasi-Fermi level for trapped electrons and trapped holes for a single species [see (21), (22), (30), and (31)] apply equally well here to a particular species. Figure 3 shows the occupancy of the traps before and after illumination for three different species: (i) $R(1)$; (ii) $R(2)<R(1)$; (iii) $R(3)>R(1)$. [The dot-dash curve represents the Fermi-Dirac distribution (corresponding to equilibrium conditions), which is the same for all three species.]

E. Varying Ratio of Electron-Trap Cross Section to Hole-Trap Cross Section

In the previous sections we have seen that each species of traps is associated with a unique set of demarcation lines and quasi-Fermi levels for trapped electrons and holes. Consider now the case of a monotonic variation of species with energy, i.e., every trap level is associated with a different species. This means that each trap will have associated with it its own demarcation lines and quasi-Fermi levels for trapped electrons and holes. If there are many levels involved, this

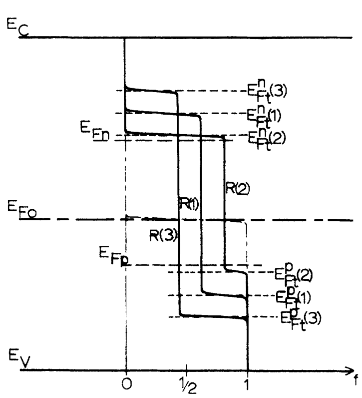

FIG. 3. Occupational functions for three different trap species.

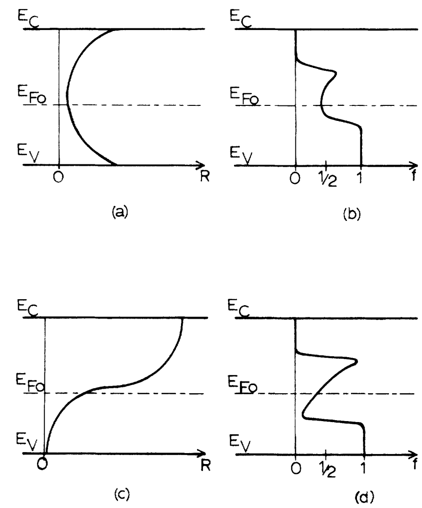

FIG. 4. Diagrams (a) and (c) illustrate two functional forms of $R(E)$, and (b) and (d) the corresponding occupational functions.

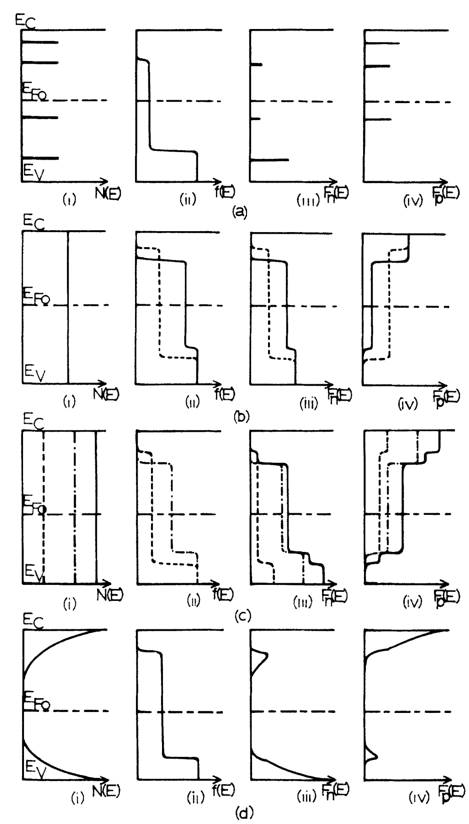

FIG. 5. Several occupancy-filling energy diagrams for trap systems (constant species). See text for further details.

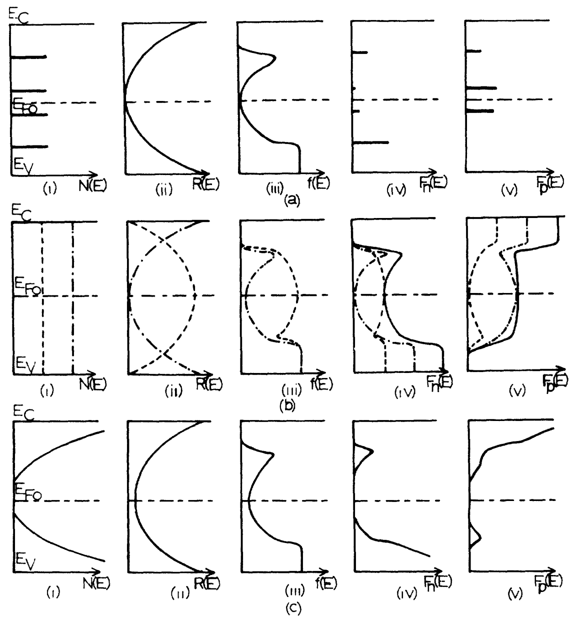

FIG. 6. Several occupancy-filling energy diagrams for trap systems (varying species). See text for further details.

method of characterizing the statistical properties of the traps is cumbersome. If one can indeed associate a functional dependence of R on energy, say $R(E)$, then it is more convenient to use $R(E)$ in (13) where appropriate. This provides a *single* occupational function for describing the system; however, one cannot associate with this function demarcation lines and trap quasi-Fermi levels for trapped electrons and holes. In Fig. 4 we illustrate the occupancy for two functional forms of $R(E)$.

F. Electron- and Hole-Energy Density for a System of Arbitrary Trap Densities and Capture Cross Sections

Figures 5 and 6 show several occupancy–filling energy diagrams for trap systems which might be encountered in practice. Figure 5 is concerned with species which are independent of energy (i.e., that have a constant value of R in the energy gap). Figure 6 is concerned with trap species which are a function of energy.

a. Constant species. Figure 5(a)(i) illustrates the case of four discrete trap levels in the energy gap of an insulator. It is assumed that all the traps belong to the same species; hence the occupancy of each is described by the same function [see Fig. 5(a)(ii)]. The electron and hole fillings [$F_n(E)$ and $F_p(E)$] are shown in Figs. 5(a)(iii) and 5(a)(iv), respectively.

Figure 5(b)(i) illustrates the case of a uniform trap distribution throughout the energy gap. The full lines in Figs. 5(b)(ii)–(iv) represent $f(E)$, $F_n(E)$, and $F_p(E)$, respectively, for a particular species, say $R(1)$. The dotted lines in Figs. 5(b)(ii)–(iv) represent $f(E)$, $F_n(E)$, and $F_p(E)$, respectively, for the case where the traps are characterized by a different species $R(2)$ such that $R(2) < R(1)$.

Figure 5(c)(i) depicts an insulator with two uniform distributions of traps $N_1(E)$ and $N_2(E)$, corresponding to two different species of traps characterized by $R(1)$ and $R(2)$, respectively [$R(1) > R(2)$]. In Fig. 5(c)(i)–(iv) the dot-dash lines refer to $N(E)$, $f(E)$, $F_n(E)$, and $F_p(E)$ for the species described by $R(1)$. The dotted line refers to these quantities for the species described by $R(2)$, and the full line in Fig. 5(c)(i), (iii), (iv) represents the total values of $N(E)$, $F_n(E)$, and $F_p(E)$, respectively. It will be noted that the resultant electron and hole fillings (full line) in Fig. 5(c)(ii)–(iv) exhibit *two* abrupt changes at the quasi-Fermi levels of the occupancy functions corresponding to the two species, $R(1)$ and $R(2)$. This fact can be generalized in the case of uniform trap distributions by the statement that for every species present there will be an abrupt change in the occupation function both above and below E_{F0}.

Figure 5(d)(i) shows a trap distribution exponentially decreasing with energy measured with respect to the band edges. This is a trap distribution corresponding to the postulated "density-of-states tail"[6] which is typically found in amorphous solids. Figure 5(d)(ii)–(iv) show for a single species (constant cross-section ratio), the occupancy and the electron and hole fillings [($F_n(E)$ and $F_p(E)$)], respectively. It is seen that $F_n(E)$ and $F_p(E)$ become peaks at their respective quasi-Fermi levels for trapped electrons and holes and only reflect the trap distribution towards the center of the energy gap, where the occupancy function is essentially constant. The electron filling in the upper half of Fig. 5(d)(iii) is interesting because of its abrupt almost discrete nature.

Similar remarks also pertain to the hole filling in the lower half of Fig. 5(d)(iv). This filling very much resembles that of a discrete trap. Because of this, it is easy to infer erroneously the existence of discrete traps in experiments which require optical stimulation prior to the observation of trapping phenomena (e.g., thermally stimulated conductivity[13]).

b. Varying species. Figure 6(a)–(c)(i)–(v) illustrate the parameters $N(E)$, $R(E)$, $f(E)$, and $F_n(E)$ and $F_p(E)$, respectively, for three trap distributions when the ratio $R(E)$ has some *functional* dependence on the position of the traps in the energy gap. Figure 6(a) illustrates the parameters for discrete traps and a ratio $R(E)$ which is rapidly decreasing from both band edges towards the center of the energy gap. As a result $f(E)$ and hence

$F_n(E)$ also decrease sharply towards the center of the energy gap. It is seen that $F_p(E)$ increases towards the center of the energy gap.

Figure 6(b) illustrates the situation for two different uniform trap distributions, $N_1(E)$ and $N_2(E)$, each distribution having its own variable ratio, $R_1(E)$ and $R_2(E)$, respectively, through the energy gap. The dash lines in Fig. 6(b) correspond to one trap distribution $[N_1(E)]$, the dot-dash lines to the other $[N_2(E)]$ and the full lines in Figs. 6(b) (iv), (v) to the resultant electron and hole fillings. It is then seen that the rapid increase of $R_1(E)$ and the rapid decrease of $R_2(E)$, as one approaches the center of the energy gap from either band edge, combine to affect the electron filling $F_n(E)$ by producing a peak around the quasi-Fermi level for trapped electrons as well as a substantial filling in the center of the energy gap. On the other hand, $F_p(E)$ shows a more or less equable filling through the energy gap because the peaking effect of $N_1(E)$ and $R_1(E)$ is smaller than that of $N_2(E)$ and $R_2(E)$.

Figure 6(c) illustrates the case for the "density-of-states tail" (exponentially decreasing from the conduction and valence bands to the center of the energy gap) characterized by a rapidly varying ratio $R(E)$. The resultant electron and hole fillings [Fig. 6(c)(iv)–(v)] are similar to but somewhat more pronounced than those of Figs. 5(d)(iii)–(iv). Once again the former remarks concerning the interpretation of peaks in $F_n(E)$ and $F_p(E)$ apply as well to Figs. 6(b)(iv) and 6(c)(iv)–(v).

G. Effect of Illumination Intensity and Temperature on Occupation Functions

Normally an increase in illumination intensity leads to an increase in the free-carrier densities. This results in the movement of the demarcation levels [see Eqs. (26) and (33)] the quasi-Fermi levels [see Eqs. (18) and (28)] for trapped electrons and holes and the quasi-Fermi levels [see Eqs. (23) and (32)] for free carriers closer to their respective band edges as shown in Fig. 7(a). For very high illumination levels it is possible to have the quasi-Fermi levels for trapped electrons and holes coincident with their respective band edges. When this occurs the occupation probability (11) is a constant value$[=\bar{n}/(\bar{n}+\bar{p})]$throughout the band gap [see Fig. 7(a)].

Decreasing the temperature has essentially the same effect upon the quasi-Fermi levels for trapped electrons and holes and demarcation levels, as that of increasing the illumination intensity. At absolute zero of temperature the parameters e_n and e_p reduce to zero with the result that the occupation probability becomes a constant value $[=\bar{n}/(\bar{n}+\bar{p})]$ throughout the band gap as shown in Fig. 7(b). This is true regardless of the intensity of the illumination.

H. Charge Neutrality Conditions

An underlying feature of the condition of uniform illumination in a solid is the existence of charge neutrality at all times. Thus for illumination levels such that the free-*excess*-carrier concentrations are far less than the trapped electrons or holes, then the number of trapped electrons in levels *above* E_{F0} is essentially equal to the trapped holes in levels *below* E_{F0}. This is illustrated by the equivalence of the cross-hatched areas in Fig. 8.

IV. DISCUSSION

Let us initially assume that all traps in the forbidden gap belong to the one particular species. Consider the traps positioned between the quasi-Fermi level for trapped electrons and the bottom of the conduction band. The rôle of these traps in the recombination process decreases exponentially with energy from the quasi-Fermi level to the band edge. Similar remarks pertain to trapping levels positioned between the top of the valence band and the quasi-Fermi level for trapped holes. Such traps are essentially in thermal equilibrium with their respective free-carrier band: in other words a free carrier falling into one of these traps would, with a high degree of certainty, be reemitted to the band from which it came. These traps are normally referred to as shallow traps.

On the other hand, *all* traps positioned between

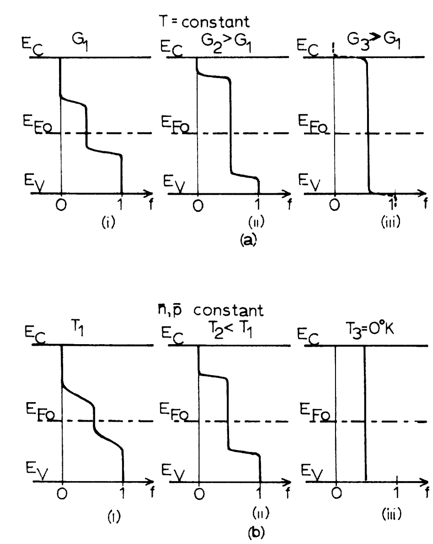

FIG. 7. Illustrations (a) (i)–(iii) represent the occupational functions for three different illumination intensities. Illustrations (b) (i)–(iii) illustrate the occupational functions for three different temperatures. Note that in (b) (i)–(iii) the distributions around the quasitrap levels E^n_{Ft} and E^p_{Ft} vary with temperature and are exaggerated for effect.

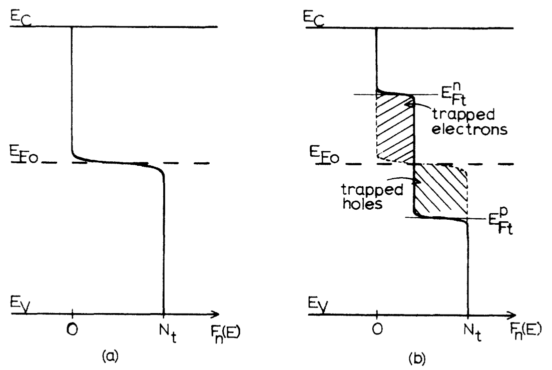

FIG. 8. Filling diagram of a solid (a) before illumination, (b) after illumination. The two cross-hatched sections are equal in area, indicating that the number of trapped electrons above E_{F0} is equal to the number of trapped holes below E_{F0}.

the two quasi-Fermi levels for trapped electrons and holes are referred to here as recombination centers. This is because the great majority of recombination traffic passes through these centers.[1] This observation is contrary to what is normally expressed in the literature[14] where the recombination efficiency is considered to be a maximum at the center of the energy gap and to decrease rapidly for higher or lower energies. Consider now those traps positioned between the quasi-Fermi level for trapped electrons E_{Ft}^n and the electron demarcation line E_{dn}. It will be recalled that an electron in a trap positioned at E_{dn} would have an equal chance of being reemitted to the conduction band or of recombining with a hole in the valence band (Sec. III C). Thus a trap positioned above E_{dn} would have a much greater probability for emitting an electron to the conduction band than of losing it to the valence band by recombination. (Similar remarks with respect to holes pertain to the traps positioned between the quasi-Fermi level for trapped holes E_{Ft}^p and the hole demarcation line E_{dp}). In contrast, recombination centers lying between the E_{dn} and E_{Ft}^p lose their electrons essentially by recombination alone. Thus when an electron from the conduction band is captured by these centers its life as a free carrier is effectively terminated. Hence, the reason for designating these traps as "electron dead states" (Fig. 9). Similarly, those recombination centers lying between E_{dp} and E_{Ft}^n are hole *dead* states (Fig. 9). In insulators where $\bar{p}$ is of the order of $\bar{n}$ in the excited state, it will be apparent from (18), (25), (26), and (33) that the quasi-Fermi levels for trapped electrons and holes are positioned very close to their respective demarcation lines [see Fig. (2)]. On the other hand, for a doped semiconductor (say n type), $\bar{n} \gg \bar{p}$ for low-level injection conditions. Also n will be approximately equal to its *equilibrium* value n_0. Thus E_{Ft}^n and E_{F0} coincide since

$$v\sigma_n N_c \exp(E_{Ft}^n - E_c)/kT = \bar{n} + \bar{p} \simeq \bar{n} \tag{38}$$

and

$$v\sigma_n N_c \exp(E_{F0} - E_c)/kT = \bar{n}_0 \ . \tag{39}$$

On the other hand, since [see (28)]

$$v\sigma_p N_v \exp(E_v - E_{Ft}^p)/kT = \bar{n} + \bar{p} \simeq \bar{n}$$

and [see (33)]

$$v\sigma_p N_v \exp(E_v - E_{dp})/kT = \bar{n} \ ,$$

then E_{dp} and E_{Ft}^p practically coincide [see Fig. 9(a)]. Because of (38) and since

$$v\sigma_n N_c \exp(E_{dn} - E_c)/kT = \bar{p} \ , \tag{40}$$

E_{dn} will normally lie well below E_{Ft}^n in energy [see Fig. 9(a)]. Between the quasi-Fermi levels for trapped electrons and trapped holes the filling of the traps, $\bar{n}/(\bar{n}+\bar{p})$, will be constant and close to unity for an n-type semiconductor [see Fig. 9(a)] and close to zero for a p-type semiconductor [see Fig. 9(b)]. Hence it follows that the traps lying in energy between the quasi-Fermi level for trapped holes and the equilibrium Fermi level are all recombination centers. However, the dead states (those recombination centers between E_{dp} and E_{dn}) will be a much smaller fraction of these recombination centers than in the case of the insulator. It follows that similar remarks pertain as well to the corresponding energy levels in a p-type semiconductor and this case is illustrated diagramatically in Fig. 9(b).

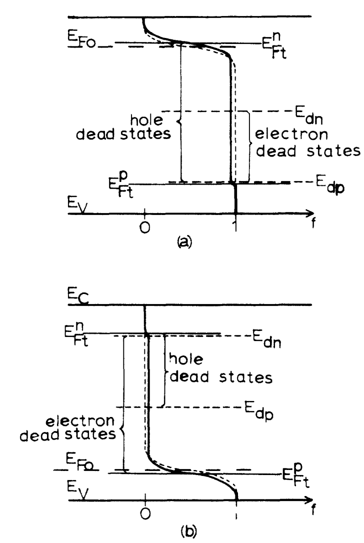

FIG. 9. Occupational functions for an arbitrary distribution of traps in (a) an n-type semiconductor and (b) a p-type semiconductor under low-level injection conditions.

In the presence of several species the above remarks apply to each individual species characterized by its own E^n_{Ft}, E^p_{Ft}, E_{dn} and E_{dp}. From the definitions of shallow traps and recombination centers, it is clear that the role of a particular trap is determined entirely by the illumination intensity G and the temperature T (see Sec. III G) because these parameters determine the positions of E^n_{Ft}, E^p_{Ft}, E_{dn} and E_{dp}. Hence it is quite possible to have an overlapping of shallow traps and recombination centers belonging to different species, as shown in Fig. 3.

There is a tendency to attempt to distinguish between a deep electron trap and a recombination center.[12] But clearly, any trap between the quasi-Fermi levels for trapped electrons and holes is a recombination center. Of course it is possible for the trap to have a very small cross section for capturing holes, which means that an electron will remain a long time in the trap, particularly if it is a dead state, before recombining with a hole. On the other hand, if the trap has a very large cross section for capturing holes, then the electron will remain only a short time in the trap before recombining with a hole. In either case, the trap is a re combination center. It thus seems appropriate to reserve the term deep trap for the description of traps in the condition of thermal equilibrium.[10] Deep electron traps would then correspond to those traps lying below E_{F0} and would be identical with shallow hole traps. Deep hole traps would be synonomous with shallow electron traps and would lie above E_{F0}.

In the past it has been considered that each group of traps having a particular electron capture cross section and a particular hole-capture cross section had to have associated with it a particular set of demarcation lines. (The use of quasi-Fermi levels for trapped electrons and trapped holes is a concept we have introduced here.) Thus, if the cross sections vary with energy, a set of demarcation lines would be required to be associated with each level under the old scheme of thinking. The concept of species will normally considerably reduce the number of sets of levels required to categorize the system. In fact, even if the cross sections vary *randomly* with energy, providing that the ratios of their cross sections are a constant in energy, *one and one only* set of demarcation lines and quasi-Fermi levels are required to categorize the system.

If the light level were sufficiently high then band-to-band recombination would occur. However it can be shown that band-to-band recombination does not affect the nonequilibrium statistics derived herein.[12]

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[2]J. Blakemore, *Semiconductor Statistics* (Pergamon, New York, 1962).

[3]A. Rose, Phys. Rev. 97, 322 (1955).

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[6]N. F. Mott, Advan. Phys. 16, 49 (1967).

[7]References 3–5 are classic examples of the efficacy of physical intuitive reasoning in the face of mathematical complexity.

[8]Note that no spin-degeneracy factor is used here. The "empty" and full conditions of a flaw will normally have different spin and orbital degeneracy choices but this is absorbed in the definition (Ref. 2) of E.

[9]If $\sigma_n = \sigma_p$, then E_t, defined by the condition $e_n = e_p$ [i.e., $N_c \exp(E_t - E_c)/kT = N_v \exp(E_v - E_t)/kT$], defines the intrinsic Fermi level E_i. Thus for $E_t > E_i$, $e_n > e_p$; and for $E_t < E_i$, $e_p > e_n$. Note that generally E_i will not be equal to E_{F0}.

[10]See J. G. Simmons, J. Phys. Chem. Solids (to be published) regarding the position of the equilibrium Fermi level in the presence of traps.

[11]If in an insulator E_{F0} lies close to either of the band edges or if the material is a doped semiconductor and the light level is relatively low, then the occupation probability will only be slightly changed (Ref. 14). For the case of an n-type semiconductor see Fig. 8(a).

[12]J. G. Simmons and G. W. Taylor (unpublished).

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