PHYSICAL REVIEW VOLUME 105, NUMBER 1 JANUARY 1, 1957

Spontaneous Radiative Recombination in Semiconductors*

WILLIAM P. DUMKE
Chicago Midway Laboratories, The University of Chicago, Chicago, Illinois

(Received September 20, 1956)

The mechanisms by which electrons and holes recombine with the emission of radiation are examined. Expressions are derived for the radiative recombination lifetimes due to direct and indirect transitions and are applied to Ge and Si. Matrix elements in the transition probability for direct and indirect transitions are obtained from analyses of the cyclotron resonance effective mass data and the optical absorption data close to the band edge, respectively. For indirect transitions the calculated lifetimes were of the order of seconds and agreed within a factor of 3 with lifetimes calculated by the method of Van Roosbroeck and Shockley. It is shown that in Ge at room temperature, while the density of filled states in the conduction band at $\mathbf{k}=0$ is very low, the rate of recombination by direct transitions is nevertheless somewhat greater than that by indirect transitions. This is consistent with the findings of Haynes. The role of radiative recombination in the observed lifetimes of excess carriers is questioned. It is concluded that for those semiconductors which have a rather high absorption constant close to the band edge (InSb), an emitted photon is usually reabsorbed before it can escape from the crystal, producing another hole-electron pair, without contributing to the macroscopically observed lifetime. In the limit of a very high absorption constant, this emission and absorption of photons acts as an additional mechanism for the diffusion of hole-electron pairs.

1. INTRODUCTION

RADIATIVE recombination of electrons and holes in semiconductors has been of interest from several points of view. Several years ago it was considered quite possible that in the available semiconductors such as Ge and Si, the lifetimes of injected carriers might be radiation limited and that therefore lifetimes could not be improved by improving the metallurgy of such semiconductors. The theory of Van Roosbroeck and Shockley[1] allowed one to calculate the radiative lifetime in a semiconductor with a specific carrier density if one knew the absorption spectrum and dielectric constant of that material. This theory was based on statistical considerations and did not take into account any details of the recombination mechanism. Van Roosbroeck and Shockley concluded that for Ge (and this would be even more true for Si because of its greater band gap) the radiation-limited lifetimes were far in excess of lifetimes yet observed and that some other nonradiative recombination mechanism must be responsible for the short observed lifetimes.

Also of interest are the recombination radiation spectra which have been observed for several semiconductors[2,3] including Ge and Si. These are of interest not only because of the mere possibility of observing such radiation, but also because of what light they may cast upon the band structure of semiconductors. The first observed radiation spectra on Ge and Si were smooth functions of wavelength with a single maxima slightly above the absorption edge, and it was suggested by Herring[4] that this radiation was the result of phonon-assisted indirect transitions between the valence and conduction bands. Recently Haynes[5] has found a second peak at 1.52 μ in the intensity of recombination radiation from Ge, indicating the existence of another radiative recombination mechanism. Also, Dash and Newman[6] have observed a very sharp rise in the absorption constant at this wavelength. From our knowledge of the band structure of Ge,[7–10] it is reasonable to ascribe both effects to the onset of direct transitions between the valence band and the conduction band at $\mathbf{k}=0$.

It is our purpose in this paper to derive expressions for the radiative recombination lifetimes based upon a microscopic analysis of both direct and indirect transitions. We shall then apply these expressions to Ge and Si and compare our results with the radiative lifetimes calculated by the method of Van Roosbroeck and Shockley in order to test the consistency of the calculations and of the physical model on which they are based. Because of misconceptions appearing in the literature concerning the relationship of the radiative recombination lifetime to the observed lifetime of excess carriers in semiconductors, we shall also examine and discuss the connection between these lifetimes.

The types of band structure we shall be considering are those for which the valence and conduction band extrema do not occur at the same point or points in the reduced Brillouin zone, and for which therefore the threshold for direct transitions is above that for indirect transitions. Most of the well-known semiconductors are of this type. Germanium and silicon both have warped degenerate valence bands at $\mathbf{k}=0$, but the conduction minima are out along the $\langle 1,1,1\rangle$ and

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* This research was supported by the U. S. Air Force, through the Office of Scientific Research of the Air Research and Development Command.

[1] W. van Roosbroeck and W. Shockley, Phys. Rev. **94**, 1558 (1954).

[2] J. R. Haynes and H. B. Briggs, Phys. Rev. **86**, 647 (1952).

[3] R. Newman, Phys. Rev. **91**, 1313 (1953).

[4] C. Herring, Phys. Rev. **93**, 943 (1954).

[5] J. R. Haynes, Phys. Rev. **98**, 1866 (1955).

[6] W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

[7] F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953).

[8] F. Herman, Physica **20**, 801 (1954).

[9] G. F. Dresselhaus, thesis, Berkeley, 1955 (unpublished).

[10] Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955).

$\langle 1,0,0\rangle$ axes in $\mathbf{k}$ space, respectively.[10] InSb is generally attributed to have its conduction minima at $\mathbf{k}=0$,[11,12] but it is quite likely that the valence band extrema lie elsewhere.[12,13]

The total rate of radiative recombination of electrons and holes may be written

$$\frac{dn}{dt}=-\sum_{if}\mathcal{P}_{if}=-(n+n_0)(p+p_0)\langle\mathcal{P}_{if}\rangle, \tag{1}$$

where $n=p$ is the number of excess electrons or holes, n_0 and p_0 are the equilibrium carrier concentrations, and $\langle\mathcal{P}_{if}\rangle$ is an average of the transition probability taken over the hole and electron distributions. To obtain the net recombination rate we must subtract the term in n_0p_0 giving the equilibrium recombination rate, which is just balanced by the blackbody production of hole-electron pairs. For a small perturbation in the equilibrium carrier concentrations, we may write

$$dn/dt=-(n_0+p_0)\langle\mathcal{P}_{if}\rangle\cdot n. \tag{2}$$

$\mathcal{P}_{if}$ will in general contain energy, momentum, and spin conservation conditions. Except for these conditions, we shall assume in what follows that matrix elements between bands are essentially constant over the hole and electron distributions, which are contained in small regions of the Brillouin zone.

The solution of Eq. (2) is $n=n(t=0)e^{-t/\tau_R}$, where

$$\tau_R=1/[(n_0+p_0)\langle\mathcal{P}_{if}\rangle]. \tag{3}$$

Our problem will be essentially to evaluate $\langle\mathcal{P}_{if}\rangle$ for the two recombination mechanisms mentioned previously.

2. INDIRECT RECOMBINATION

Indirect recombination is a two-step process involving both an optical transition and phonon scattering.[14] Since optical transitions in semiconductors occur essentially vertically in $\mathbf{k}$ space, a phonon collision is required to take the electron either to a virtual state n above the valence maximum from which it may drop down optically (Figs. 1 and 2), or to the valence maximum from a virtual state n' above the conduction minimum. Energy is conserved in the total process, the energy difference between the initial and final states being equal to the photon energy plus or minus the phonon energy, depending upon whether a phonon is created or annihilated in the scattering. The probability per unit time for an indirect transition from an initial conduction band state i to a final valence band state f through intermediate states n and n' is given by the usual expression for a second-order transition[15] as

$$\mathcal{P}_{if}=\frac{2\pi}{\hbar}\rho(\hbar\omega)\times\left\{\sum_n\left[\frac{|H_{in}{}^{+}|^2|H_{nf}|^2}{(E_n-E_i+k\theta)^2}+\frac{|H_{in}{}^{-}|^2|H_{nf}|^2}{(E_n-E_i-k\theta)^2}\right]+\sum_{n'}\left[\frac{|H_{in'}|^2|H_{n'f}{}^{+}|^2}{(E_{n'}-E_i-\hbar\omega)^2}+\frac{|H_{in'}|^2|H_{n'f}|^2}{(E_{n'}-E_i-\hbar\omega)^2}\right]\right\}, \tag{4}$$

where $\rho(\hbar\omega)$ is the density in energy of final photon states per unit volume and is given by

$$\rho(\hbar\omega)=N_0{}^3\omega^2/\pi^2c^3\hbar, \tag{5}$$

where N_0 is the index of refraction, $H_{in}{}^{+}$ and $H_{in}{}^{-}$, etc., are electron-phonon interaction matrix elements for phonon creation and annihilation, and H_{nf} and H_{in} are matrix elements for spontaneous optical emission.

We are limited in what we can say about the matrix elements for phonon scattering. They will, however, be of the form

$$\begin{aligned}H_{in}{}^{-}&=\beta_{in}(e^{\theta/T}-1)^{-1},\\H_{in}{}^{+}&=\beta_{in}(1-e^{-\theta/T})^{-1}.\end{aligned} \tag{6}$$

The optical matrix elements can be shown to be equal to[15]

$$H_{nf}=-\frac{e}{m}\left(\frac{2\pi\hbar}{\omega}\right)^{\frac{1}{2}}P_{nf}, \tag{7}$$

where P_{nf} is the matrix element of the momentum operator between states n and f. We may immediately write an expression for the radiative recombination lifetime using Eq. (3) and taking account of the fact that electrons must conserve spin in the transition. For simplicity, we shall ignore the $k\theta$ contribution to energy denominators which is small, and also we shall consider the electron and hole distributions to be located exactly at the band edges. This is a reasonable approximation in view of the fact that $\Delta E\gg kT$, where ΔE is the band gap.

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[11] Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 556 (1955).

[12] R. W. Keyes, Phys. Rev. **99**, 490 (1955).

[13] According to the analysis of Blount, Callaway, Cohen, Dumke, and Phillips, Phys. Rev. **101**, 563 (1956), the absorption spectrum around the absorption edge in InSb (0.15 at 300°K) exhibits evidence of indirect transitions. However, H. Y. Fan and G. W. Gobeli [Bull. Am. Phys. Soc. Ser. II, **1**, 111 (1956)] report that the absorption spectra is characteristic of direct transitions with a band gap of 0.175 ev at 300°K. A comparison of the photoelectromagnetic response data of S. W. Kurnick and R. M. Zitter, J. Appl. Phys. **27**, 278 (1956) and absorption data of V. Roberts and J. E. Quarrington, J. Elec. **1**, 1952 (1955) was performed by the author to determine if the absorption between 0.15 and 0.175 ev at 300°K actually resulted in the production of conducting holes and electrons. A simple theoretical analysis ignoring surface recombination showed that the shape of the photoelectromagnetic response near the cutoff should follow essentially a $KL/(1+KL)$ law, where L is the effective diffusion length. By using this relation it was possible to accurately predict the position and shape of the observed photoelectromagnetic response edge from the absorption data, indicating that free carriers are indeed produced well below 0.175 ev.

[14] Absorption by indirect transitions is treated by Bardeen, Blatt, and Hall, *Proceedings of the Atlantic City Photoconductivity Conference, 1954* (John Wiley and Sons, Inc., New York, 1956). It is also discussed in Chicago Midway Laboratories' Technical Report, CML-TN-55-A.2-13 (unpublished).

[15] See W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, Oxford, 1944), second edition, p. 59.

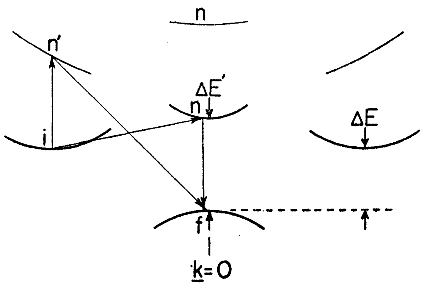

FIG. 1. Band structure favoring indirect transitions from conduction band states i to valence band states f through intermediate states n and n'. Direct transitions between higher conduction band at $\mathbf{k}=0$ and valence band may nevertheless be important.

The radiative recombination lifetime is

$$\tau_{Ri}=\frac{c^3\hbar^2m^2}{2e^2\Delta EN_0{}^3\gamma}\left(\frac{1}{n_0+p_0}\right)\left(\frac{e^{\theta/T}-1}{e^{\theta/T}+1}\right), \tag{8}$$

where γ contains all the unknowns and is given by

$$\gamma=\left\langle\sum_n\frac{|\beta_{in}|^2|H_{nf}|^2}{(E_n-E_i)^2}+\sum_{n'}\frac{|H_{in}{}'|^2|\beta_{n'f}|^2}{(E_{n'}-E_i-\hbar\omega)^2}\right\rangle.$$

Information about γ may be obtained from an indirect transition analysis of the absorption edge data. To a good approximation, absorption by indirect transitions takes the form[14]

$$K=A\left[\frac{(\hbar\omega+k\theta-\Delta E)^2}{e^{\theta/T}-1}+\frac{(\hbar\omega-k\theta-\Delta E)^2}{1-e^{-\theta/T}}\right],$$

where

$$A=\frac{1}{2\pi}\frac{\gamma e^2mN_0}{c\hbar^5\Delta E}\sum_v\alpha_v{}^{-\frac{3}{2}}\sum_c\alpha_c{}^{-\frac{3}{2}}. \tag{9}$$

Here m/α_v and m/α_c are the valence and conduction band effective masses, respectively, and the sums over v and c are over the extrema in these bands. If we substitute for γ in terms of A, Eq. (8) becomes

$$\tau_{Ri}=\frac{1}{4\pi}\frac{m^3c^2}{\hbar^3}\frac{\sum_v\alpha_v{}^{-\frac{3}{2}}\sum_c\alpha_c{}^{-\frac{3}{2}}}{A\Delta E^2N_0{}^2}\frac{1}{n_0+p_0}\frac{e^{\theta/T}-1}{e^{\theta/T}+1}. \tag{10}$$

Using this formula, we have calculated values of τ_{Ri} for Ge and Si, obtaining our value for A from the analyses of the absorption edges of Ge[16] and Si[17] by MacFarlane and Roberts. The conduction band effective masses are those given by Dresselhaus, Kip, and Kittel[10] and we assume 4 conduction band minima for Ge. The valence band effective masses are those given by Lax and Mavroides[18] for the density of states. For intrinsic Ge at room temperature ($n_0=2.4\times10^{13}$), $\tau_{Ri}=1.98$ sec, which does not compare unfavorably with the lifetime calculated by Van Roosbroeck and Shockley[1] of 0.75 sec using that part of the absorption spectra where only indirect transitions are involved. About this result we may conclude qualitatively that it supports the indirect absorption model of the absorption edge in Ge, but that there are appreciable deviations in the absorption from Eq. (9) several kT above the edge. These deviations may be due to variation of matrix elements with energy, p^4 terms in the expansion of energy around an extremum, etc. For intrinsic Si at room temperature ($n_0=1.4\times10^{10}$), $\tau_{Ri}=1.7\times10^4$ sec. For a more attainable impurity concentration in Si, of, say, $n_0+p_0=10^{15}$, $\tau_{Ri}=0.47$ sec.

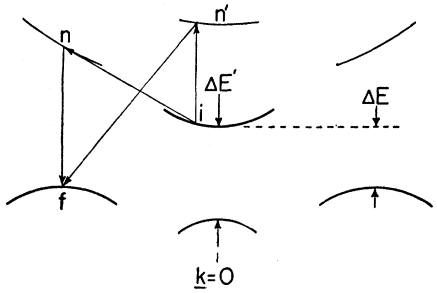

FIG. 2. Analog of band structure of Fig. 1, with roles of valence and conduction bands interchanged.

3. DIRECT RECOMBINATION

For the type of bandstructure we have assumed, a substantial recombination by means of direct transitions can occur if the energy gap for direct transitions $\Delta E'$ is not too many kT larger than the energy gap for indirect transitions. For the band structure of Fig. 1 there would in this case be a finite density of electrons in the conduction band at $\mathbf{k}=0$. This corresponds to the case of Ge for which $\Delta E'-\Delta E=0.18$ ev at 300°K.[6] Similarly, holes could be present in the valence band at $\mathbf{k}=0$ for the structure indicated in Fig. 2. We shall in the future discuss only the structure of Fig. 1, but with minor changes our results will also apply to the structure of Fig. 2. In Fig. 1 we have drawn the conduction band states at $\mathbf{k}=0$ as constituting a relative minimum because of the closeness of the valence band and the f sum rule.[19] The density of electrons in the conduction band at $\mathbf{k}=0$ can easily be calculated if we know the density of available states in the conduction band minima and assume that nearly all conduction band electrons are contained in these minima. We shall also assume that the conduction band electrons at $\mathbf{k}=0$ have a simple effective mass given by $m/\alpha_{c'}$. The density of electrons at $\mathbf{k}=0$ is

$$f_n(\mathbf{p})=\frac{n_0}{2}\left(\frac{2\pi\hbar}{mkT}\right)^{\frac{3}{2}}\left(\sum_c\alpha_c{}^{-\frac{3}{2}}\right)^{-1}\exp\left(-\frac{\Delta E'-\Delta E+\alpha_cp^2/2m}{kT}\right). \tag{11}$$

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[16] G. C. MacFarlane and V. Roberts, Phys. Rev. **98**, 1865 (1955).

[17] G. C. MacFarlane and V. Roberts, Phys. Rev. **97**, 1714 (1955).

[18] B. Lax and J. G. Mavroides, Phys. Rev. **100**, 1650 (1950).

[19] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition.

A further condition which must hold for our analysis to be valid is that the time for equilibrium between the conduction minima and relative minima electrons to occur must be small compared to the time it takes an electron in the relative minima to drop down into the valence band. Otherwise our maximum rate of decay will be limited by the rate at which electrons can be scattered into the states at $\mathbf{k}=0$. Since acoustical scattering times are on the order of 10^{-14} sec and those for atomic transitions are $\sim 10^{-8}$ sec, we shall assume this condition to be satisfied although the scattering time for a fairly large momentum change such as we require here may be several orders of magnitude larger than 10^{-14}.

The transition probability is simply

$$\mathcal{P}_{if}=\frac{2\pi}{\hbar}|H_{if}|^2\rho(\hbar\omega)\delta_{p_ip_f}, \tag{12}$$

where H_{if} and $\rho(\hbar\omega)$ have been given in the previous section. Averaging over the hole and electron distributions, we obtain

$$\begin{aligned}\langle\mathcal{P}_{if}\rangle&=\frac{1}{n_0p_0}\sum_{\mathbf{p}_c=\mathbf{p}_v}\mathcal{P}_{if}f_n(\mathbf{p}_c)f_p(\mathbf{p}_v)\\&=\frac{2\omega e^2N_0^3}{m^2c^3\hbar}|P_{if}|^2\left(\frac{2\pi\hbar^2}{mkT}\right)^{\frac{3}{2}}\\&\quad\times\exp\left(-\frac{\Delta E'-\Delta E}{kT}\right)\frac{\sum_v(\alpha_{c'}+\alpha_v)^{-\frac{3}{2}}}{\sum_c\alpha_c^{-\frac{3}{2}}\sum_v\alpha_v^{-\frac{3}{2}}}.\end{aligned} \tag{13}$$

We may immediately write down the lifetime for direct recombination by using Eq. (3) and rearranging some terms.

$$\begin{aligned}\tau_{Rd}&=\frac{1}{2(2\pi)^{\frac{3}{2}}}\left(\frac{m^{7/2}c^3k^{\frac{3}{2}}}{\hbar e^2}\right)\left(\frac{T^{\frac{3}{2}}}{\Delta E'^2N_0^3|P_{if}|^2}\right)\\&\quad\times\exp\left(\frac{\Delta E'-\Delta E}{kT}\right)\frac{\sum_c\alpha_c^{-\frac{3}{2}}\sum_v\alpha_v^{-\frac{3}{2}}}{\sum_v(\alpha_{c'}+\alpha_v)^{-\frac{3}{2}}}\left(\frac{1}{n_0+p_0}\right).\end{aligned} \tag{14}$$

Equation (14) applies also to the elementary band model of semiconductors, for which direct transitions occur at the band edge, if we let $\Delta E'=\Delta E$ and $\alpha_{c'}=\alpha_c$. For Ge, $\alpha_{c'}$ and P_{if} may be estimated from our knowledge of its band structure,[8–10] and the cyclotron resonance data for holes.[10] In the absence of spin-orbit splitting, there would be 6 valence bands in Ge and these would be degenerate at $\mathbf{k}=0$. As a result of spin-orbit splitting, two of these bands have energies 0.3 ev below the other four at $\mathbf{k}=0$. Away from $\mathbf{k}=0$ the upper four bands are split into two doubly-degenerate bands, the states of which have warped surfaces of constant energy in the Brillouin zone and which correspond to the light and heavy hole bands. An analysis of these bands may be made by using basis functions which transform like p-type wave functions times a spin wave function and setting up the perturbation matrix between these wave functions and wave functions for higher lying states. Transforming the matrix to the J, M_J representation in which the spin-orbit energy is diagonal, one may then diagonalize the perturbation energy and also solve for the new eigenfunction as linear combinations of the p-like wave functions.

From the cyclotron resonance data it is possible to calculate the second-order perturbation energy between the p-like basis functions and the higher lying bands of various symmetries. The largest contribution is that due to the conduction band state at $\mathbf{k}=0$, partially due to its closeness in energy. According to Dresselhaus,[9] the matrix element between one of the valence-band basis functions $\epsilon_1{}^+$ and the conduction-band wave function β^- of the perturbation $\mathbf{p}\cdot\mathbf{P}/m$ is numerically given by

$$|(\epsilon_1{}^+|\mathbf{P}|\beta^-)|^2=|(\epsilon_1{}^+|P_x|\beta^-)|^2=28.6(2\Delta E'/m).$$

Expressing the wave functions for the valence bands in terms of these basis functions and averaging over the possible polarizations of the emitted photon, one finds that the optical matrix element for transitions between the lowest conduction band at $\mathbf{k}=0$ and either the light hole band or the heavy hole band is given by

$$|P_{if}|^2=1/3|(\epsilon_1{}^+|\mathbf{P}|\beta^-)|^2.$$

$\alpha_{c'}$ is given by the f sum rule,[19]

$$\alpha_{c'}=1+\frac{2}{m}\sum_i\frac{|\mathbf{P}_{c'v_i}|^2}{E_{c'}-E_{v_i}}. \tag{15}$$

One can easily show that the sum of the contributions from the heavy hole and light hole bands is $|\mathbf{P}_{c'v_1}|^2+|\mathbf{P}_{c'v_2}|^2=2/3|(\epsilon_1{}^+|\mathbf{P}|\beta^-)|^2$. Also, for the split-off valence band $|\mathbf{P}_{c'v_3}|^2=1/3|(\epsilon_1{}^+|\mathbf{P}|\beta^-)|^2$. Because this band is 0.3 ev below the other two valence bands, its contribution to the f sum will be somewhat reduced. Following Dresselhaus,[9] we estimate

$$\alpha_{c'}=1+\left(\frac{2}{3}+\frac{1}{3}\frac{0.81}{0.81+0.30}\right)28.6=27, \tag{16}$$

corresponding to an effective mass of 0.037 m.

Substituting these values in Eq. (14) and using a value of 0.18 ev for $\Delta E'-\Delta E$ from the data of Dash and Newman,[6] we find the lifetime for direct radiative recombination in intrinsic Ge at 300°K to be $\tau_{Rd}=0.29$ sec. Haynes,[5] and Burstein, Picus, and Teitler[20] have calculated the radiative recombination lifetime for both direct and indirect transitions in Ge and have obtained 0.25 sec and 0.30 sec, respectively. For indirect transition $\tau_{Ri}=0.75$ sec, so that if we solve for

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[20] Burstein, Picus, and Teitler (unpublished).

the direct transition lifetime using the relation that

$$1/\tau_R = 1/\tau_{Ri} + 1/\tau_{Rd}, \tag{17}$$

we find that Haynes' result corresponds to 0.38 sec and that of Burstein, Picus, and Teitler to 0.50 sec, for the lifetime due to only direct transitions, in reasonable agreement with our result. This agreement can be cited as additional support for the current model of the energy bands in Ge, and for the analysis of the cyclotron resonance data.

The exponential dependence of the lifetime on T^{-1} in Eq. (14) reflects the dependence of the direct recombination rate on the number of electrons at $\mathbf{k}=0$ in the conduction band. When Haynes[5] observed the recombination spectrum of Ge at 300°K, he was barely able to detect the direct recombination component. At higher temperatures one would expect this component to become more prominent due to the larger fraction of electrons at $\mathbf{k}=0$. Because $\Delta E' - \Delta E$ for Si is at least 1.4 ev one would not expect to observe any radiation due to direct recombination in Si.

4. CONNECTION BETWEEN RADIATIVE AND OBSERVED LIFETIMES

Frequently, in the literature,[21,22] it is suggested that radiative recombination is a factor fundamentally limiting the maximum obtainable lifetimes of excess carriers in certain semiconductors. There is a certain degree of justifiability in this position for semiconductors such as Ge and Si for which the absorption coefficient K is fairly low (~ 10 cm^{-1}) for several kT above the absorption edge. In this case, an emitted photon has a good chance of escaping the crystal before being reabsorbed with the resulting production of another hole electron pair. For Ge and Si however, the radiative recombination lifetime is quite long and other recombination mechanisms must be invoked to account for the much shorter lifetimes actually observed.

It is a mistake, however, to suppose that there is any close connection between radiative recombination and observed lifetimes for semiconductors which have high absorption constants close to the band edge. This will be particularly true of semiconductors in which direct transitions occur either at or near the band edge. In such materials K will be on the order of 10^3 for energies corresponding to the majority of the emitted photons. Since the transitions are not between localized states, we do not obtain a degradation of the photon energy by the Franck-Condon principle. While it is true τ_R may be small and of the order of observed lifetimes for these materials, except for the radiation originating within a distance of approximately $1/K$ from the surface, none of the recombination radiation can escape, and consequently no net decrease in the number of hole electron pairs due to radiative recombination is observed. Therefore, except for thin films, one would not expect to find radiation limited semiconductors. Even in the case in which the carriers are initially produced on the surface of a thick specimen, it may be shown that the observed lifetime of these carriers due to radiative recombination is infinite.

When K is large, there will be a diffusion of hole electron pairs from a region where they are more dense and more photons are released to a region of lower density where they may be absorbed. We shall calculate the diffusion constant for such a process and show that it is quite small. We shall be considering only the radiation due to recombination of the excess carriers, since the radiation from the equilibrium distributions will be in equilibrium with the blackbody background. Consider now a smoothly varying distribution of excess carriers given by $n(x)$, and let us calculate the flux of photons across a plane of unit cross section at $x=0$. Let $P(E)dE$ be the probability that a photon is in the energy interval dE. The number of photons of energy in dE being emitted from a layer dx thick is $n(x)dxP(E)dE/\tau_R$ and of these $(ndxPdEK/\tau_R)e^{-Kl}dl$ will be reabsorbed within dl a distance l away from the initial point of their production. A fraction $(l-|x|)/2l$ for $l \geq |x|$ will cross the plane at $x=0$. We shall expand $n(x)$ in a Taylor series about $x=0$ and throw away all but the first two terms. Since the constant term can give no net flux across $x=0$ we shall ignore it also. The net flux is

$$\begin{aligned} d\Phi &= \frac{KPdE}{2\tau_R}\left(\frac{\partial n}{\partial x}\right)_{x=0}\left[\int_{-\infty}^{0} x\int_{|x|}^{\infty}\frac{l-|x|}{l}e^{-Kl}dldx \right. \\ &\qquad\qquad \left. -\int_{0}^{\infty} x\int_{|x|}^{\infty}\frac{l-|x|}{l}l^{-Kl}dldx\right], \\ d\Phi &= -\frac{PdE}{K^2\tau_R}\left(\frac{\partial n}{\partial x}\right)_{x=0}\cdot\int_0^{\infty} z\int_z^{\infty}\frac{L-z}{L}e^{-L}dLdz, \\ &= -\frac{1}{3}\frac{PdE}{K^2\tau_R}\left(\frac{\partial n}{\partial x}\right)_{x=0}. \end{aligned} \tag{18}$$

The total flux of photons of all energies is

$$\begin{aligned} \Phi &= -\frac{1}{3\tau_R}\left(\frac{\partial n}{\partial x}\right)_{x=0}\int P(E)\frac{dE}{K^2} \\ &= -\frac{1}{3\tau_R}\langle K^{-2}\rangle\left(\frac{\partial n}{\partial x}\right)_{x=0}, \end{aligned} \tag{19}$$

corresponding to a diffusion coefficient $(1/3\tau_R)\langle K^{-2}\rangle$. The average of K^{-2} over the indirect radiation spectra diverges at the absorption band edge, so that a lower limit corresponding to $=1/L$, where L is of the order of the sample dimensions, is necessary. Radiation for $K<1/L$ includes the radiation which escapes from the crystal. The average of K^{-2} over the direct transition

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[21] J. W. Allen and I. M. Mackintosh, J. Elec. **1**, 138 (1955).

[22] J. S. Moss and J. H. Hawkins, Phys. Rev. **101**, 1609 (1956).

spectra does not diverge. An idea of the magnitude of this photon diffusion coefficient can be had using $\tau=10^{-3}$, $\langle K^{-2}\rangle=3\times10^{-3}$, giving an effective diffusion coefficient of 1 cm^2/sec corresponding to a carrier mobility of 40 cm^2/volt sec at room temperature, which is quite small compared to actual mobilities.

ACKNOWLEDGMENTS

In conclusion, I would like to acknowledge stimulating discussions with S. W. Kurnick and F. F. Rieke. It was in the course of these conversations that many of the ideas contained in this paper first occurred to the author.

PHYSICAL REVIEW VOLUME 105, NUMBER 1 JANUARY 1, 1957

Extension of the Thomas-Fermi-Dirac Statistical Theory of the Atom to Finite Temperatures

R. D. Cowan, *Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico*

AND

J. Ashkin, *Carnegie Institute of Technology, Pittsburgh, Pennsylvania*

(Received September 14, 1956)

The Thomas-Fermi theory of the atom is generalized to include the effects of temperature as well as exchange. This leads to a nonlinear integral equation for the Fermi electron-momentum distribution function, and the usual Poisson equation for the electron-density distribution. Analytical solutions of the integral equation are given for the limiting cases of near-degeneracy and complete nondegeneracy, and a numerical method of calculating solutions in the intermediate case is described. A complete discussion of the thermodynamics of the atom is given; in particular, it is shown that the Gibbs free energy is the product of the number of electrons and the electronic chemical potential (Fermi energy), despite statements which have been made to the contrary. Numerical results have verified the virial theorem for all Z, T, and atomic volumes. The ratio of the calculated energy for $T=\mathcal{P}=0$ to the experimental total ionization energy varies from 2.07 for H down to 1.33 for Al, and is presumably still closer to unity for higher-Z elements. Some numerical results are given for iron over the density range 0.1 to 10 times normal and for values of kT from 0 to 1000 ev. Pressures, energies, and entropies are lower than the corresponding values calculated without exchange by as much as 40% at $kT=10$ ev, by up to 10% at $kT=100$ ev, and by only negligible amounts at $kT=1000$ ev.

1. INTRODUCTION

THE Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) statistical models of the atom[1–3] have been extensively used as the basis for approximate calculations of the equations of state of compressed materials.[4–6] The original Thomas-Fermi model has been extended in two directions—first by taking into account exchange effects at zero temperature[2–5] and second by allowing nonzero temperatures but neglecting exchange.[5–7]

Some attempts have been made to include the effects of both exchange and elevated temperatures. Umeda and Tomishima[8] have done this by deriving a temperature-perturbation type of Thomas-Fermi equation[6] in which the effects of exchange are taken into account by using an effective temperature[9] which minimizes the Helmholtz free energy. Ashkin[10] has generalized the Thomas-Fermi-Dirac theory (with exchange), obtaining equations applicable for any temperature. However, his solution, obtained by an analytical perturbation procedure, is (like Umeda and Tomishima's valid only to temperatures of a few volts (1 volt≅11 605.6°K). The present paper is an extension of this early work (including the perturbation solution), and also outlines a method by which accurate solutions may be calculated for arbitrarily high temperatures.

2. THEORY

A. Basic Integral Equation and Associated Differential Equation for the Charge Density

The application of the statistical theory of the atom to equation-of-state calculations is well known, but for

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