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Possible Mechanism for Radiationless Recombination in Semiconductors

LEON BESS
Philco Corporation, Philadelphia, Pennsylvania

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A set of two Auger-type processes has been found by which the trapping of a hole or electron can occur with the emission of an energetic hole or electron instead of a photon. A rough calculation is made of the cross section of the combination of the two processes as well as the cross section of the radiative process. For a wide class of semiconductors, it is found that the combination of the radiationless processes will predominate over the radiative one under practically all operating conditions.

I. INTRODUCTION

THERE seems to be increasing evidence in the study of semiconductors that minority and majority carriers can recombine without the emission of electromagnetic radiation. Thus far, the only possible process by which this could have occurred is one where there is a simultaneous emission of a large number (from 10 to 100) of phonons. Rough perturbation calculations, however, seem to show that such a multiphonon process is highly improbable and thus will not be able to compete with the radiation process under most conditions.

In this paper another nonradiative recombination scheme will be proposed which, according to the rough calculations to be presented here, may not only compete with but even overwhelm the radiative process. The recombination scheme will consist of two types of processes, each of which resemble the Auger effect in atomic physics since each process will allow a hole or electron to be trapped with the emission of another energetic free hole or electron instead of an infrared or light quantum. In each case, after emission, the energetic hole or electron will rapidly lose its excess kinetic energy through collisions with lattice centers and other free carriers until it is moving with only thermal energy. Thus, it is seen that the excess energy in these trapping processes eventually will be converted into heat instead of a photon as in the radiative process.

The recombination mechanism will be assumed to be a two-step process involving a deep trap as described by Shockley and Read.[1] The first step of this process (which will be referred to by the subscript e in all subsequent symbols) consists of an electron in the conduction band jumping into an empty trap. The second step of the process (to be referred to by the subscript h) consists of an electron in a filled trap jumping into a vacancy in the valence band. (This is usually called the trapping of a hole.)

In the subsequent sections, rough order-of-magnitude calculations will be made of the cross sections of all the radiationless processes as well as the radiative one. The treatment will be based on three main assumptions. These are: (a) the solid can be treated as a dielectric medium (having the static dielectric constant ϵ_0) in which mobile carriers move as though they were free particles having an effective mass m^*, (b) a hydrogen-like model can be used for a deep trap, and (c) all quantum calculations can be done within the Born approximation. The justification of some of these assumptions will be dealt with in the subsequent sections.

After calculating the cross sections, the probability of occurrence for each type of process will then be compared in both steps of the recombination process. Finally, some brief remarks will be made on how the radiationless recombination process described here should behave under various doping conditions and this will be compared with the Shockley-Read theory.

II. RADIATIONLESS PROCESS NO. 1

This process will be treated in detail only for the second step of the recombination mechanism although, as will be shown subsequently, the calculation can easily be adapted to the first step.

In the process to be considered, a free hole moving with thermal velocity will approach a filled trap when there are free electrons also near the trap. It will then be possible for a transition to occur where one of the electrons (i.e., either the electron in the trap or one of the free electrons) will annihilate the hole and the other electron will be ejected into the conduction band with a kinetic energy nearly equal to the energy difference (E_T-E_V) between the trap energy, E_T, and the top of the valence band, E_V.

It should be mentioned that the foregoing recombination process cannot occur when the free hole encounters two free electrons because it will not be possible for momentum to be conserved. With one of the electrons trapped, the momentum deficiency can easily be absorbed by the trapping center which is a heavy atom.

The general expression for a cross section can be found in various quantum mechanics texts and is of the form[2]

$$d\sigma=\frac{w}{v_0}=\frac{2\pi L^3}{\hbar v_0}|(b,e|H_i|f,h)|^2\rho_F, \tag{1}$$

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[1] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).

[2] See, for example, W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, London, 1947), second edition, p. 90. The notation used in the remainder of this paper will follow that of Heitler.

where $d\sigma$ is the differential cross section; L^3 is the total volume of the semiconductor crystal; ρ_F is the density of the final state and has the form

$$\rho_F = L^3 p m^* d\Omega_p/(2\pi\hbar c)^3, \tag{2}$$

where p is the momentum of the energetic free electron and m^* is its effective mass; $d\Omega_p$ is solid angle of its emission direction; v_0 is the velocity of the hole.

The quantity $(b,e|H_i|f,h)$ is the matrix element for the process and has the form

$$(b,e|H_i|f,h) = \int\int u_{\text{II}}^*(\mathbf{r}_1,\mathbf{r}_2) H_i u_{\text{I}}(\mathbf{r}_1,\mathbf{r}_2) d^3r_1 d^3r_2. \tag{3}$$

The process has been considered to be essentially a two electron interaction with the hole of the being viewed as a vacancy in a valence electron state. $\mathbf{r}_1$ is the space coordinate of the free electron and $\mathbf{r}_2$ is the space coordinate of the trapped electron. The space parts of the initial and final total wave function $u_{\text{I}}(\mathbf{r}_1,\mathbf{r}_2)$ and $u_{\text{II}}(\mathbf{r}_1,\mathbf{r}_2)$, respectively, appearing in Eq. (3) have the form

$$u_{\text{I}}(\mathbf{r}_1,\mathbf{r}_2) = (1/\sqrt{2})[u_b(\mathbf{r}_1)u_n(\mathbf{r}_2) \pm u_b(\mathbf{r}_2)u_n(\mathbf{r}_1)], \tag{4a}$$

$$u_{\text{II}}(\mathbf{r}_1,\mathbf{r}_2) = (1/\sqrt{2})[u_f(\mathbf{r}_1)u_h(\mathbf{r}_2) \pm u_f(\mathbf{r}_2)u_h(\mathbf{r}_1)]. \tag{4b}$$

The $(+)$ or $(-)$ sign occur in Eq. (4) above depending on whether the two electrons have antiparallel spins or parallel spins (i.e., on whether they form a singlet or triplet system). The functions, u_b, u_n, u_f, and u_h, are the space parts of the wave functions, ψ_b, ψ_n, ψ_f, and ψ_h, which will be in the form of reduced Bloch wave functions:

$$\psi_b(\mathbf{r},t) = \frac{B(\mathbf{b}_0)}{(\pi a_t^3)^{\frac{1}{2}}} \exp\left\{\left(\frac{i}{\hbar c}\right)\left[\mathbf{b}_0\cdot\mathbf{r} - \left(E_0 + \frac{\Delta E}{2}\right)t\right] - \frac{r}{a_t} + i(E_C - E_T)\left(\frac{t}{\hbar c}\right)\right\}, \tag{5a}$$

$$\psi_f(\mathbf{r},t) = \frac{B(\mathbf{b}_0)}{L^{\frac{3}{2}}} \exp\left\{\left(\frac{i}{\hbar c}\right)\left[\mathbf{b}_0\cdot\mathbf{r} - \left(E_0 + \frac{\Delta E}{2}\right)t\right] + \left(\frac{i}{\hbar c}\right)\left[\mathbf{p}\cdot\mathbf{r} - \frac{p^2 t}{2m^*c^2}\right]\right\}, \tag{5b}$$

$$\psi_h(\mathbf{r},t) = \frac{B(\mathbf{b}_0)}{L^{\frac{3}{2}}} \exp\left\{\left(\frac{i}{\hbar c}\right)\left[\mathbf{b}_0\cdot\mathbf{r} - \left(E_0 - \frac{\Delta E}{2}\right)t\right] + \left(\frac{i}{\hbar c}\right)\left[\mathbf{p}_0\cdot\mathbf{r} - \frac{p_0^2 t}{2m^*c^2}\right]\right\}, \tag{5c}$$

$$\psi_n(\mathbf{r},t) = \frac{B(\mathbf{b}_0)}{L^{\frac{3}{2}}} \exp\left\{\left(\frac{i}{\hbar c}\right)\left[\mathbf{b}_0\cdot\mathbf{r} - \left(E_0 + \frac{\Delta E}{2}\right)t\right]\right\}. \tag{5d}$$

$B(\mathbf{b}_0)$ is the periodic block factor which is assumed not to vary rapidly with $\mathbf{b}_0$; $\mathbf{b}_0$ is the Brillouin zone momentum vector, and E_0 is its corresponding mean energy value; ΔE is the width of the energy band gap.

ψ_b of Eq. (5a) is the wave function of the trapped electron. The trap model assumed here is a hydrogenlike structure in a dielectric material with the effective dielectric constant, ϵ, adjusted so that the ionization energy is equal to $(E_C - E_T)$. (E_C is the edge of the conduction band.) This means that the "radius," a_t, of the trap is determined by the relation

$$a_t = [E_R/(E_C - E_T)]^{\frac{1}{2}} a_H, \tag{6}$$

where E_R is the Rydberg energy of hydrogen and a_H is the Bohr radius.

ψ_f of Eq. (5b) is the wave function for the energetic free electron in the conduction band.

ψ_h is the wave function for the incident hole and ψ_n is the wave function for one of the free electrons in the vicinity of the trap. (The thermal energy of the free electron has been neglected in this rough treatment.) Since a hole is to be assumed to be a vacancy in the valence band, ψ_h corresponds to a valence band state of an electron, thus explaining the $(E_0 - \frac{1}{2}\Delta E)$ energy factor instead of $(E_0 + \frac{1}{2}\Delta E)$.

H_i in Eq. (1) is the interaction energy, which will be chosen on the assumption that only the longitudinal components of the electromagnetic field contribute to the reaction. Thus, only the instantaneous Coulombic interaction between two electrons need be considered (since with the hole being merely an electron vacancy, this will be a two-electron problem).

In order to obtain a finite value for the cross section, it will be necesssary for the Coulombic interaction to have a kind of screening radius only within which interaction can take place between two free carriers in the semiconductor. Such a screening radius has been proposed by Pines[3] on quite general grounds. The value of this screening radius was proposed to be the Debye length, L_D.

Thus, H_i will be assumed to have the following form:

$$H_i = \frac{e^2}{\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|} \exp(-|\mathbf{r}_1 - \mathbf{r}_2|/L_D), \tag{7}$$

where ϵ_0 is the static dielectric constant.[4]

When one uses the relations of Eq. (7) and equation sets (4) and (5) in Eq. (3), the matrix element can be

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[3] D. Pines, in *Solid State Physics, Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 377.

[4] It has been assumed in this and the subsequent sections that the effective dielectric constant of the Coulombic interactions between moving electrons and holes is nearly ϵ_0. This is felt to be justified because within the critical separation distance of 10^{-7} cm the two carriers would be moving past so rapidly that the interaction would be of the order of 10^{-14} second. This, however, would have nearly all frequency components less than the critical value of $(\Delta E/\hbar)$ ($\cong 10^{15}$ sec^{-1}) at which the effective dielectric constant starts to decrease.

shown[5] to have the form:

$$(b,e|H_i|f,h)=32\pi(e^2/\epsilon_0)(L_D{}^2a_t{}^{\frac{3}{2}}/L^{9/2})\times[F(p_0L_D)F^2(|\mathbf{p}-\mathbf{p}_0|a_t)\pm F(|\mathbf{p}-\mathbf{p}_0|L_D)F^2(p_0a_t)], \quad (8)$$

where $F(x)\equiv[1+x^2]^{-1}$.

If Eqs. (2) and (8) are substituted in Eq. (1) and the result is integrated over $d\Omega_p$, the expression for the total cross section, σ_{1h}, will become:

$$\sigma_{1h}(p_0)=4\pi(16L_D{}^2/a_H)^2(pm^*/\epsilon_0{}^2p_0m)(a_t{}^3N_e)\times[F^2(p_0L_D)F^4(pa_t)+F^2(pL_D)F^4(p_0a_t)-F(p_0L_D)F(pL_D)F^2(p_0a_t)F^2(pa_t)]. \quad (9)$$

The result of Eq. (9) has been averaged over electron spin directions, with a statistical weight of 1 being given to the singlet state and of 3 to the triplet state.

Moreover, the parameter, N_e, is the free electron volume density in the semiconductor and appears in Eq. (9) because of the fact that it is possible for any free electron in the semiconductor to be in the vicinity of the trap. Thus, the cross section for one electron must be multiplied by N_eL^3. Since the cross section for one electron will contain the factor L^{-3}, the L^3's will cancel and the result will be that of Eq. (9).

Incidentally, from equation set (4), it can be deduced that the following energy relation must be satisfied for energy to be conserved and, therefore, for the reaction to take place.

$$p_0{}^2/2m^*c^2-(E_C-E_T)+\Delta E=p^2/2m^*c^2. \quad (10)$$

It is also possible for a reaction similar to the one described above to take place in the first step of recombination. Here the role of holes and electrons would be reversed and an energetic hole would be given off instead of an energetic electron. The details of the calculation of the cross section, σ_{1e}, would be very similar to those of σ_{1h}; and within the accuracy adopted here,

$$\sigma_{1e}(p_0)=\sigma_{1h}(p_0)[N_h/N_e], \quad (11)$$

N_h is the hole concentration.

Incidentally, it should be mentioned that there is another process, similar to process No. 1, which can take place in the second recombination step. This process, instead of involving a free electron and a free hole near a trap, would involve an exciton (i.e., the solid state analog of positronium) coming within the vicinity of the trap and being annihilated. However, by using the calculation methods developed here, it can be shown[6] that this exciton process will ordinarily not be able to compete with the two radiationless processes presented here for the very low density of excitons usually present in most semiconductors.

III. RADIATIONLESS PROCESS NO. 2

This process will first be considered here in connection with the first step of recombination. The treatment of the second step will be shown to be very similar. The process consists of a free electron approaching an empty trap when there are other free electrons also near the trap. It will then be possible for a free electron to jump into the trap with the energy excess (E_C-E_T) being taken up in the kinetic energy of another free electron in the vicinity. As can be seen, the calculation can be made into a two-electron problem just as in Sec. II and the details will be very similar to those of process No. 1.

The actual value of the matrix element for this type of process will be quite different than that of process No. 1. Instead of equation set (4), u_{I} and u_{II} will now have the following form:

$$u_{\mathrm{I}}(\mathbf{r}_1,\mathbf{r}_2)=(1/\sqrt{2})[u_e(\mathbf{r}_1)u_n(\mathbf{r}_2)\pm u_e(\mathbf{r}_2)u_n(\mathbf{r}_1)], \quad (12a)$$

$$u_{\mathrm{II}}(\mathbf{r}_1,\mathbf{r}_2)=(1/\sqrt{2})[u_b(\mathbf{r}_1)u_f(\mathbf{r}_2)\pm u_b(\mathbf{r}_2)u_f(\mathbf{r}_1)]. \quad (12b)$$

Here u_n, u_b and u_f have the same definitions as before. u_e, representing the spare part of the wave function for the incident free electron, can be derived from ψ_e which is of the form:

$$\psi_e(\mathbf{r},t)=\frac{B(\mathbf{b}_0)}{L^{\frac{3}{2}}}\exp\left\{\left(\frac{i}{\hbar c}\right)\left[\mathbf{b}_0\cdot\mathbf{r}-\left(E_0+\frac{\Delta E}{2}\right)t+\mathbf{p}_0\cdot\mathbf{r}-\frac{p_0{}^2t}{2m^*c^2}\right]\right\}. \quad (13)$$

From equation set (12), Eq. (13), and Eq. (8) it can readily be seen that the matrix element, $(e,n|H_i|b,f)$, for process No. 2 will have the same form as $(b,n|H_i|f,h)$ in Eq. (8) except that $\mathbf{p}$ must be substituted for $\mathbf{p}_0$ and $\mathbf{p}_0$ for $\mathbf{p}$. By using this result and proceeding in a similar manner used in process No. 1, the result for the cross section $\sigma_{2e}(p_0)$ can be obtained by substituting p for p_0 in all of the F's in Eq. (9). The expression for $\sigma_{2e}(p_0)$ will then be:

$$\sigma_{2e}(p_0)=4\pi\left(16\frac{\hbar^2}{p^2a_H}\right)^2\left(\frac{pm^*}{\epsilon_0p_0m}\right)(a_t{}^3N_e)F^4(pa_t). \quad (14)$$

It has been assumed in deriving Eq. (14) that $pL_D\gg1$. In comparing the result of Eq. (14) with that of Eq. (9) it will be found that $\sigma_{2e}(p_0)$ is, in general, much smaller than $\sigma_{1h}(p_0)$. This is due to the fact that $F(p_0L_D)$ in Eq. (8) is much larger than the corresponding $F(pL_D)$ in Eq. (13).

For the second step of recombination it is possible for a process similar to the one just described to occur. The role played by the two free electrons before would now be played by two free holes. The details of the calculation of the cross section σ_{2h} would be very similar to those of σ_{2e} and within the accuracy adopted here,

$$\sigma_{2h}(p_0)=\sigma_{2e}(p_0)(N_h/N_e). \quad (15)$$

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[5] See Appendix A for the details of the calculation. The contribution resulting from the factor $|B(\mathbf{b}_0)|^2$ being different from unity has been neglected.

[6] Exciton annihilation at a trap has been calculated by Y. Toyozawa [Progr. Theoret. Phys. Japan **12**, 421 (1954)] using entirely different methods. However, the two results seem to compare within an order of magnitude.

It will be noticed that in all the calculations up to now the wave functions for free particles were assumed to be plane waves (i.e., all of the calculations have been made only within the Born approximation).

In the case of the wave functions for the emitted energetic free particles, the plane-wave assumption is obviously fairly good since here the particle kinetic energy is comparable to the ionization energy of the trap. It is also a good assumption for wave functions of low-energy incident particles where the trap is initially filled (i.e., in the calculation of σ_{1h} and σ_{2h}), since then the trap site will be electrically neutral and there will be no interaction with the incident particle.

It is only for low-energy incident particles where the trap is initially unfilled (i.e., in calculating σ_{1e} and σ_{2e}) that the plane wave approximation for the wave functions may not be valid since here there will be a Coulombic interaction between the incident particles with the kinetic energy of the particles far less than the ionization energy of the trap. It is not expected that this discrepancy will greatly affect the results of the calculation of σ_{1e}. The main reason for this is that the wave-function amplitude would deviate significantly from its plane-wave value only in a region of volume around the trap whose magnitude is about πa_t^3. However, the significant contribution to the integral [written in Eq. (2A)] which is involved in the matrix element of Eq. (8) will be from a volume region much greater than πa_t^3, and any corrections within the region of πa_t^3 can be neglected.

The situation just described is not true for the matrix element integral in Eq. (13). Here nearly all of the significant contributions to the integral occur within a volume region of πa_t^3. Thus, it can be expected that the local fluctuations in the incident particle wave function amplitude may greatly affect the result of σ_{2e}. However, the plane wave approximation will nevertheless be used here for the calculation of σ_{2e} because, first (as will be seen later), an error in this cross section will not greatly affect the total lifetime. Second, in order to be able to make an accurate calculation which is to have any significance, it is necessary to have an accurate model of a deep trap (the hydrogenlike model used here is obviously not correct) and this is not known. It might be mentioned that if one uses the hydrogenlike trap model in an accurate calculation (which is closely related to the calculation of hydrogen ionization by electron impact), the result will be a cross section significantly lower than that calculated by the Born approximation.

IV. RADIATIVE PROCESS

In order to be able to compare the frequency of occurrence of the radiationless processes with the radiative one, it is necessary to calculate the cross section for the occurrence for the first and second steps of recombination with the emission of a photon.

For the second recombination step, this is done by using the cross-section formula of Eq. (1), where v_0 now is the velocity of a free hole and ρ_F takes the form

$$\rho_F = \frac{\epsilon_0^{\frac{3}{2}} L^3 k^2 d\Omega_k}{(2\pi\hbar c)^3}, \tag{16}$$

where k is the energy of the quantum and $d\Omega_k$ is the infinitesimal solid angle defining its direction of emission.

The factor $\epsilon_0^{\frac{3}{2}}$ appears in Eq. (16) because, as stated above, the crystal is assumed to be a dielectric medium for radiation frequencies less than $(\Delta E/\hbar)$. Thus, the wave vector will be $(\epsilon_0)^{\frac{1}{2}}\mathbf{k}$ instead of $\mathbf{k}$ as in free space. The interaction Hamiltonian will then take the form

$$H_i = (e\hbar/\epsilon_0 mc)\mathbf{A}_\mathrm{T}\cdot\nabla. \tag{17}$$

The initial and final wave functions in the calculation of the matrix element will be of the form of Eq. (5a) and Eq. (5c), respectively. Making the appropriate substitutions in Eq. (1), the details of the calculation will then closely resemble those of the photoelectric effect and can be found in standard quantum mechanics texts.[7] The differential cross section $d\sigma_{rh}$ which is then obtained is

$$d\sigma_{rh} = (32\times 137)\left(\frac{c}{v_0}\right)\left(\frac{e^2}{mc^2}\right)^2 \times \frac{(\hbar c/a_t)^5[k/\epsilon_0^{\frac{1}{2}}](\mathbf{b}_0\cdot\boldsymbol{\varepsilon}_k)^2 d\Omega_k}{[(\hbar c/a_t)^2 + (\mathbf{p}_0 - \epsilon_0^{\frac{1}{2}}\cdot\mathbf{k})^2]^4}, \tag{18}$$

where $\boldsymbol{\varepsilon}_k$ is the unit polarization vector of the quantum. After summing over the quantum polarization and performing the $d\Omega_k$ integration (assuming that $p_0 \gg k$), the total cross section σ_{rh} is:

$$\sigma_{rh}(p_0) \cong \left(\frac{\pi}{3}\right)\left(\frac{\hbar}{mc}\right)^2\left(\frac{c}{v_0}\right)\left(\frac{2ka_t^2}{\epsilon_0^{\frac{1}{2}} a_0 \hbar c}\right) F^4(p_0 a_t), \tag{19}$$

where a_0 is the atomic spacing so that $b_0 \cong 3\hbar c/a_0$ and where it has been assumed that:

$$k \cong E_C - E_T. \tag{20}$$

The calculation of σ_{re} will for the most part be very similar to σ_{rh} and it can be shown that

$$\sigma_{re}(p_0) = \left(\frac{E_C - E_T}{E_T - E_V}\right)\sigma_{rh}(p_0). \tag{21}$$

V. COMPARISON OF THE PROCESSES

If it is assumed that the percentage of empty traps (whose concentration is N_t) is ξ, then it can be shown that the decay rate for electrons is:

$$dN_e/dt = N_e\xi(1/\tau_{re} + 1/\tau_{ce}), \tag{22}$$

where

$$\frac{1}{\tau_{re}} = N_t \int_0^\infty g(p_0;T) v_0 \sigma_{re}(p_0) dp_0, \tag{23}$$

$$\frac{1}{\tau_{ce}} = N_t \int_0^\infty g(p_0;T) v_0 [\sigma_{1e}(p_0) + \sigma_{2e}(p_0)] dp_0. \tag{24}$$

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[7] See, for example, reference 2, p. 122.

Here $g(p_0; T)$ is the Maxwellian thermal distribution in $p_0(=m^* v_0)$ corresponding to the temperature T.

Upon carrying out the integrations over p_0 in Eqs. (23) and (24), the approximate result will be

$$1/\tau_{re} \cong \tfrac{2}{3} N_t \bar{v}_0 \bar{\sigma}_{re}, \tag{25}$$

$$\frac{1}{\tau_{ce}} \cong \tfrac{2}{3} N_t \bar{v}_0 \left[\left(\frac{L_D}{\bar{L}_D}\right)\left(\frac{N_h}{N_i}\right)\bar{\sigma}_{1e} + \left(\frac{N_e}{N_i}\right)\bar{\sigma}_{2e} \right], \tag{26}$$

where $\bar{v}_0 = (3kT/m^*)^{\frac{1}{2}}$; N_i the intrinsic carrier concentration and $\bar{L}_D$ is the Debye length at intrinsic concentration. From Eqs. (9), (14), and (19) the definition for the various $\bar{\sigma}$'s are:

$$\bar{\sigma}_{re} = \left(\frac{\pi}{3}\right)\left(\frac{\hbar}{mc}\right)^2\left(\frac{m^* c}{\bar{p}_0}\right)\left[\frac{a_t^2 \bar{k}}{(\epsilon_0)^{\frac{1}{2}} a_0 \hbar c}\right] F^4(\bar{p}_0 a_t), \tag{27a}$$

$$\bar{\sigma}_{1e} = 4\pi(16a_t)^2 \left(\frac{a_t \bar{L}_D}{\epsilon_0^2 a_H^2}\right)\left(\frac{\bar{p}}{\bar{p}_0}\right)\left(\frac{m^*}{m}\right) \times \left[\left(\frac{\hbar c}{\bar{p}_0}\right)^3 N_i\right] F^4(\bar{p} a_t), \tag{27b}$$

$$\bar{\sigma}_{2e} = 4\pi(16a_t)^2 \left(\frac{a_t \hbar}{\epsilon_0^2 a_H^2 \bar{p}}\right)\left(\frac{\bar{p}}{\bar{p}_0}\right)\left(\frac{m^*}{m}\right) \times \left[\left(\frac{\hbar c}{\bar{p}}\right)^3 N_i\right] F^4(\bar{p} a_t). \tag{27c}$$

The parameters $\bar{p}_0$, $\bar{p}$, and $\bar{k}$ are defined from the following approximate relationships

$$\bar{p}_0 = m^* \bar{v}_0, \tag{28a}$$

$$\bar{p} = [2m^*(E_C - E_T)c^2]^{\frac{1}{2}}, \tag{28b}$$

$$\bar{k} = E_C - E_T. \tag{28c}$$

To compare the frequency of occurrence of the radiationless processes with the radiative one, it is necessary to obtain the ratio (τ_{re}/τ_{ce}). When the ratio is greater than unity, the radiationless processes will predominate. To compute this ratio, it is necessary to know the cross-section ratios $(\bar{\sigma}_{1e}/\bar{\sigma}_{re})$ and $(\bar{\sigma}_{2e}/\bar{\sigma}_{re})$. The cross-section ratio can be shown as a function of the various physical parameters by using equation set (27). The result is:

$$\left(\frac{\bar{\sigma}_{1e}}{\bar{\sigma}_{re}}\right) = 3\times 4^5 \left[\frac{mc^2 \bar{p} a_0}{\epsilon_0^{\frac{3}{2}} \bar{k} \hbar c}\right]\left[\frac{a_t \bar{L}_D}{a_H^2}\right] \times \left[\left(\frac{\hbar c}{\bar{p}_0}\right)^3 N_i\right] \frac{F^4(\bar{p} a_t)}{F^4(\bar{p}_0 a_t)}, \tag{29}$$

$$\left(\frac{\bar{\sigma}_{2e}}{\bar{\sigma}_{re}}\right) = 3\times 4^5 \left[\frac{mc^2 a_0 a_t}{\epsilon_0^{\frac{3}{2}} \bar{k} a_H^2}\right]\left[\left(\frac{\hbar c}{\bar{p}}\right)^3 N_i\right] \frac{F^4(\bar{p} a_t)}{F^4(\bar{p}_0 a_t)}. \tag{30}$$

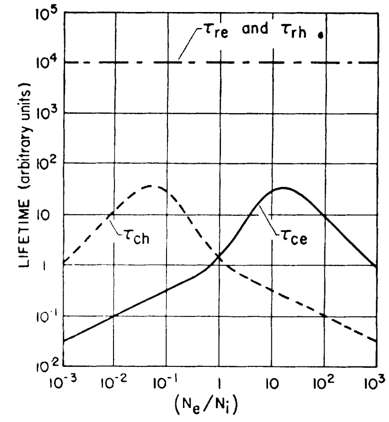

FIG. 1. Radiative and nonradiative lifetime parameters *vs* doping for germanium at 300°K.

Comparison of the various processes by means of numerical calculations will now be made for the case of germanium at 300°K. The values for the various physical parameters used in the calculations will be: $\Delta E = 0.7$ ev; $E_C - E_T = 0.3$ ev; $m^*/m = 0.3$, $a_t = 3\times 10^{-8}$ cm; $a_0 = 1.7\times 10^{-8}$ cm; $\bar{L}_D = 3\times 10^{-5}$ cm; $\hbar c/\bar{p}_0 = 1.7 \times 10^{-7}$ cm, $\hbar c/\bar{p} = 5\times 10^{-8}$ cm; $N_i = 3\times 10^{13}$ cm^{-3}, and $\epsilon_0 = 16$. When these values are used in Eqs. (29) and (30), it can be found that $(\bar{\sigma}_{1e}/\bar{\sigma}_{re})$ is about 10^4 whereas $(\bar{\sigma}_{2e}/\bar{\sigma}_{re})$ is only about 5. The actual values of the cross sections found from equation set (27) are $\bar{\sigma}_{re} \cong 2\times 10^{-20}$ cm^2; $\bar{\sigma}_{2e} \cong 10^{-19}$ cm^2 and $\bar{\sigma}_{1e} \cong 2\times 10^{-16}$ cm^2 (which is about the value found experimentally[8]).

As can be seen from Eq. (26), the nonradiative lifetime τ_{ce} will be a function of doping. The dependence is illustrated in Fig. 1 (by the solid line) and is based on the calculations performed above for germanium. In calculating values for the curves in Fig. 1, it has been assumed that L_D will depend on doping as given in the following relation:

$$L_D = [\epsilon_0 kT / 2\pi e^2 (N_e + N_h)]^{\frac{1}{2}} = \bar{L}_D [2N_i/(N_e + N_h)]^{\frac{1}{2}}. \tag{31}$$

In studying the τ_{ce} curve of Fig. 1, it should be noted that the variation of τ_{ce} with doping when the sample is p-type is relatively small [varying only as $(N_e/N_i)^{\frac{1}{2}}$]. This is because in this range (where the No. 1 type of recombination process predominates) the variation of L_D with doping tends to counteract the variations of τ_{ce}.

As the sample is made n-type, τ_{ce} will at first increase rapidly because now the variation of L_D with doping will be in the same direction as the variation of τ_{ce}. The increase in τ_{ce} with doping will however change to a decrease for highly doped n-type samples when the No. 2 type of recombination process becomes dominant.

The treatment for the second step of recombination is almost exactly the same as the first step and the results are very similar.

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[8] Burton, Hall, Morin, and Severiens, J. Phys. Chem. 57, 853 (1953).

Instead of Eqs. (25) and (26), the following results for the second-step lifetimes τ_{rh} and τ_{ch} can be obtained

$$1/\tau_{rh}=\tfrac{3}{2}N_t\bar{v}_0\bar{\sigma}_{rh}, \tag{32}$$

$$\frac{1}{\tau_{ch}}=\tfrac{3}{2}N_t\bar{v}_0\left[\left(\frac{L_D}{\bar{L}_D}\right)\left(\frac{N_e}{N_i}\right)\bar{\sigma}_{1h}+\left(\frac{N_h}{N_i}\right)\bar{\sigma}_{2h}\right]. \tag{33}$$

The forms of $\bar{\sigma}_{rh}$, $\bar{\sigma}_{1h}$ and $\bar{\sigma}_{2h}$ will be exactly the same as their counterparts $\bar{\sigma}_{re}$, $\bar{\sigma}_{1e}$ and $\bar{\sigma}_{2e}$ in equation set (27) except that the definitions for $\bar{p}$ and $\bar{k}$ will be changed. These will become:

$$\bar{p}=[2m^*c^2(E_T-E_V)]^{\frac{1}{2}}, \tag{34a}$$

$$\bar{k}=(E_T-E_V). \tag{34b}$$

The dotted curve in Fig. 1 shows how τ_{ch} will vary with doping. As can be seen, the τ_{ch} curve is just the τ_{ce} curve rotated about the $(N_e/N_i=1)$ line. This means that τ_{ch} in the n region will behave similar to τ_{ce} in the p region (and *vice versa*) and the arguments for this behavior are the same as those for τ_{ce}.

The long dashed line in Fig. 1 represents the curve for τ_{re} and τ_{rh}. As can be seen, even at the most unfavorable points (corresponding to the "humps" in the τ_{ce} and τ_{ch} curves), τ_{re} and τ_{rh} are about 300 times as great as τ_{ce} or τ_{ch}. This means that the nonradiative recombination processes are always greatly predominant over the radiative ones.

VI. GENERAL REMARKS ON THE THEORY

In this section some very brief, descriptive remarks will be made on some of the physical aspects of the theory described above.

The first question to be considered concerns the characteristics of semiconductors that would tend to favor radiative transitions over the type of nonradiative transitions described here. As can be seen from Eqs. (22), (24), (23), and (26), the rate of decay by a radiative transition is linearly proportional to the carrier concentrations N_e or N_h whereas the rate of radiationless transitions will be proportional to the $\frac{3}{2}$ power or second power of these quantities. Thus, it would appear that radiative transitions would be more prevalent in high resistivity material where N_e and N_h are relatively small. Moreover, from a study of Eqs. (29) and (30) it can be seen that the ratios $(\bar{\sigma}_{1e}/\bar{\sigma}_{re})$ and $(\bar{\sigma}_{2e}/\bar{\sigma}_{re})$ will decrease rapidly when $\bar{p}a_t>1$ owing to the factor $F^4(\bar{p}a_t)$ ($\bar{p}_0a_t$ is, in general, less than unity). Now, according to Eqs. (6) and (28b), $\bar{p}a_t$ will be independent of the trap depth (E_C-E_T) in the first step of recombination. However, Eq. (6) is valid only for donor types of traps. For acceptor types, (E_C-E_T) in Eq. (6) must be replaced by (E_T-E_V). In this case, $\bar{p}a_t$ will be proportional to the quantity $[(E_C-E_T)/(E_T-E_V)]^{\frac{1}{2}}$ which, for a given trap "depth" (E_T-E_V), will become larger as the band gap ΔE increases. Thus, it seems likely that $\bar{p}a_t>1$ and $(\bar{\sigma}_{1e}/\bar{\sigma}_{re})$ and $(\bar{\sigma}_{2e}/\bar{\sigma}_{re})$ can be small only in wide-band-gap materials. By a similar argument it can be shown that this is also true for $(\bar{\sigma}_{1h}/\bar{\sigma}_{rh})$ and $(\bar{\sigma}_{2h}/\bar{\sigma}_{rh})$. Therefore, it would seem that a wide band gap should be characteristic for semiconductors with a relatively high prevalence of radiative transitions. The fact that most phosphors are high-resistivity wide-band-gap materials seems to lend validity to the above remarks.

The second question to be considered is how the recombination scheme described here would modify the Shockley-Read theory.[1] The only point of difference with the Shockley-Read theory is that the lifetime parameters τ_{ce} and τ_{ch} are functions of doping whereas the corresponding quantities ($1/C_n$ and $1/C_p$) of the Shockley-Read theory are not.

The difference in the two theories would show in the actual lifetime, τ, *vs* doping characteristic (Fig. 2 of reference 1).

From Eq. (5.5) of reference 1, the dependence of the lifetime, τ, on various parameters will be

$$\tau=\tau_{ch}(N_e+\bar{N}_e)/(N_e+N_h)+\tau_{ce}(N_h+\bar{N}_h)/(N_e+N_h), \tag{35}$$

where $\bar{N}_e$ and $\bar{N}_h$ correspond to n_1 and p_1 (in reference 1) respectively. Upon using the results of Fig. 1 in Eq. (35), it can be seen that variation of τ with doping for the nonradiative processes considered here should be quite similar to the characteristic illustrated in Fig. 2 (of reference 1). The main reason for this is that when the sample is n type the first term in Eq. (35) will, in general, be dominant and in this range τ_{ch} will have only a small variation with doping (whereas in the Shockley-Read theory τ_{p0} was constant with doping). Similarly, when the sample is p type the second term in Eq. (35) will be dominant and in this range τ_{ce} will only vary slowly with doping. The variation of τ_{ce} in the n region (and τ_{ch} in the p region) will not, in general, greatly affect the τ *vs* doping characteristic. The difference between the two theories should show up mainly at high doping concentrations where in the Shockley-Read theory the lifetime, τ, will be constant with the doping ratio (N_e/N_i); whereas according to the theory presented here, there would be a slight falling off of the lifetime as the sample became more highly doped [the variation would be as $(N_i/N_e)^{\frac{1}{2}}$ or $(N_i/N_h)^{\frac{1}{2}}$]. From the existing experimental evidence,[8] it appears to be rather difficult to decide which condition actually prevails.

In the above treatment the nonradiative recombination process was compared only to the radiative recombination process involving traps. It is also possible for radiative recombination to occur involving a band to band transition. Under quasi-equilibrium conditions this latter type of radiative recombination has been calculated by several investigators to be very infrequent (corresponding to a lifetime of the order of one second in germanium). However, under conditions of large concentrations of both types of carriers (such as in a *p-n* junction for large forward voltages), the band-to-band radiative recombination would be expected (from the above theory) to be more prevalent with respect to the nonradiative processes. This is because the band-to-band radiative transition would vary as the square of the carrier concentration (actually as N_eN_h) whereas the radiationless transitions would, in general, vary only as the $\frac{3}{2}$ power of the carrier concentration. Band-to-band radiation has actually been observed in a *p-n* junction under forward voltage by Haynes.[9]

It should be mentioned that the fact that the Auger effect could be important in recombination has previously been stated by several authors.[10,11] There has been no detailed calculation, but it would appear that only the processes corresponding to $\bar{\sigma}_{2e}$ or $\bar{\sigma}_{2h}$ (i.e., only the radiationless process No. 2) had actually been considered. The calculations performed here, however, would indicate that, in general, it is only the radiationless process No. 1 that is prevalent enough to be able to give rise to the observed semiconductor recombination.

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APPENDIX A

By using Eqs. (9), set (4), and set (5) in Eq. (3), the matrix element can be shown to have the form

$$(b,n|H_i|f,h)=e^2(\pi a_t^3)^{-\frac{1}{2}}L^{-9/2}[I(r_1/a_t;\,p_0r_2|pr_1)\pm I(r_1/a_t;\,p_0r_1|pr_2)], \quad (1\text{A})$$

where

$$I(r_1/a_t;\,p_0r_2|pr_1)=\int\int\frac{d^3r_1d^3r_2}{|\mathbf{r}_1-\mathbf{r}_2|}\times\exp\left[\frac{1}{\hbar c}\left(-\frac{|\mathbf{r}_1-\mathbf{r}_2|}{L_D}-\frac{r_1}{a_t}+i\mathbf{p}_0\cdot\mathbf{r}_2-i\mathbf{p}\cdot\mathbf{r}_1\right)\right]. \quad (2\text{A})$$

Below, use may also be made of the relations

$$I(r_2/a_t;\,p_0r_1|pr_2)\equiv I(r_1/a_t;\,p_0r_2|pr_1), \quad (3\text{A})$$

$$I(r_2/a_t;\,p_0r_2|pr_1)\equiv I(r_1/a_t;\,p_0r_1|pr_2). \quad (4\text{A})$$

There remains only, therefore, the problem of evaluating the integral $I(r_1/a_t;\,p_0r_2|pr_1)$. The following substitutions must be made in Eq. (2A):

$$\mathbf{r}_1=(1/\sqrt{2})(\mathbf{u}+\mathbf{v}), \quad (5\text{A})$$

$$\mathbf{r}_2=(1/\sqrt{2})(\mathbf{u}-\mathbf{v}), \quad (6\text{A})$$

so that $d^3ud^3v=d^3r_1d^3r_2$. Equation (2A) will then become

$$I=\frac{1}{\sqrt{2}}\int_\infty\frac{d^3v}{v}\exp\left[\frac{1}{\hbar c}\left(i\sqrt{2}\mathbf{p}_0\cdot\mathbf{v}-\frac{\sqrt{2}v}{L_D}\right)\right]\int_\infty d^3u\times\exp\left[\frac{1}{\hbar c}\left(\frac{i}{\sqrt{2}}(\mathbf{p}_0-\mathbf{p})\cdot(\mathbf{u}-\mathbf{v})-\frac{|\mathbf{u}-\mathbf{v}|}{\sqrt{2}a_t}\right)\right]. \quad (7\text{A})$$

Since in the u integration $\mathbf{v}$ will act as a constant vector and the integration is over all space, the substitution

$$\mathbf{z}=\mathbf{u}-\mathbf{v}, \quad d^3z=d^3u,$$

can be made in Eq. (7A) and will become a product of two independent integrals. When one performs the ϕ angular integration in both integrals I will become:

$$I=\frac{(2\pi)^2}{\sqrt{2}}\left\{\int_0^\infty vdv\int_{-1}^1dx_1\exp\left[\frac{v}{\hbar c}\left(i\sqrt{2}p_0x_1-\frac{\sqrt{2}}{L_D}\right)\right]\right\}\times\left\{\int_0^\infty z^2dz\int_{-1}^1dx_2\times\exp\left[\frac{z}{\sqrt{2}\hbar c}\left(i|\mathbf{p}_0-\mathbf{p}|x_2-\frac{1}{\sqrt{2}a_t}\right)\right]\right\}, \quad (8\text{A})$$

where $x_1=\cos\theta_1$ and $x_2=\cos\theta_2$. When one performs the x_1 and x_2 integrations, the result is:

$$I=\frac{(4\pi)^2}{\sqrt{2}\mathbf{p}_0|\mathbf{p}_0-\mathbf{p}|}\left\{\int_0^\infty dv\exp\left(-\frac{\sqrt{2}v}{L_D}\right)\sin\left(\frac{\sqrt{2}p_0v}{\hbar c}\right)\right\}\times\left\{\int_0^\infty zdz\exp\left(\frac{-z}{\sqrt{2}a_t}\right)\sin\left(\frac{|\mathbf{p}_0-\mathbf{p}|z}{\sqrt{2}\hbar c}\right)\right\}. \quad (9\text{A})$$

When one performs the v and z integrations, the final result is then:

$$I\left(\frac{r_1}{a_t};\,p_0r_2|pr_1\right)=\frac{2(4\pi)^2(\hbar c)^2}{(\hbar c/L_D)^2+p_0^2}\cdot\frac{(\hbar c/a_t)(\hbar c)^3}{[(\hbar c/a_t)^2+|\mathbf{p}-\mathbf{p}_0|^2]^2}. \quad (10\text{A})$$

When one uses the result of Eqs. (10A), (3A), and (4A) in Eq. (1A), the expression will then become that of Eq. (10) in the text.

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