Radiative Capture by Impurities in Semiconductors*

J. S. BLAKEMORE
Florida Atlantic University, Boca Raton, Florida
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Detailed balance arguments are used to study the relationship between photo-ionization cross section and radiative-capture cross section for transitions between conduction-band states and the ground state of a localized flaw; the existence of a spectrum of excited states, of compensating impurities, and of competing processes does not impede the development of a simple relationship. This relationship can be expressed in a way which illustrates that the capture lengths of an interacting photon and an interacting electron are in inverse proportion to their respective momenta. It is noted that the reciprocity of photo-ionization and radiative recombination can be utilized either to evaluate recombination in terms of known optical properties *or* to deduce optical density in terms of known recombination cross sections, and examples of both procedures are given. The thermally averaged capture cross section is expressed as a weighted integral of the photo-ionization cross section with respect to energy, and it is shown how the temperature dependence of radiative recombination is related to the spectral dependence of the photo-ionization cross section.

I. INTRODUCTION

THE creation and annihilation of free carriers in a semiconductor proceed through a variety of energy-transformation mechanisms, at rates dependent on the intrinsic and extrinsic properties of the medium, the temperature, fluxes of photons and phonons, and the boundary conditions. In this morass of competing processes, a very useful tool is the knowledge that any process and its inverse balance in detail at thermal equilibrium. The conclusions drawn from detailed balance arguments can be applied (with appropriate reservations) to characterizing the behavior when nonequilibrium sets of carrier densities are imposed.

Detailed balance was used by van Roosbroeck and Shockley[1] in determining the carrier lifetime for band-to-band radiative recombination from a knowledge of the intrinsic optical-absorption spectrum in a semiconductor. Their approach, which was shown by Bowlden[2] to be valid whether or not phonon cooperation is required for the radiative transition, has been applied to band-to-band situations in a variety of semiconducting materials.

Our purpose in this paper is an examination of some of the consequences of the van Roosbroeck–Shockley approach for an *extrinsic* transition, comparing the photo-ionization cross section σ_i of a localized flaw with its radiative capture cross section σ_r. Use of this approach in considering bound-free transitions in a semiconductor has been surprisingly limited, even though it is the normal procedure for the analogous problems in atomic physics—such as the astrophysical problem of a large partially ionized cloud of hot atomic hydrogen.[3]

The detailed balance approach was followed by Sclar and Burstein[4] in ascertaining how efficient localized flaws with hydrogenic wave functions would be in radiative recombination. However, the connection between spontaneous and stimulated transition coefficients can be explained regardless of the bound-state wave function. As Landsberg has noted,[5] this connection can be used either for a better understanding of recombination or for a better understanding of the macroscopic optical properties.

II. THE DETAILED RADIATIVE BALANCE

In order to be specific, we shall consider the radiative interaction within a homogeneous semiconducting medium of monovalent donors with the conduction band. This band is supposedly characterized by an isotropic and energy-independent effective mass m_c; then at energy E above the base of the band the density of states is[6]

$$g(E)=4\pi(2m_c/h^2)^{3/2}E^{1/2}. \tag{1}$$

We shall assume that the conduction-electron distribution is a thermal Fermi one whether or not excess carriers have been created; then the fraction of occupied states at energy E is

$$f_c(E)=[1+\exp((E-\phi_0)/kT)]^{-1}. \tag{2}$$

The conduction electron quasi-Fermi level ϕ_c is synonymous with the Fermi level ϕ at equilibrium, when $f_c \rightarrow f_{c0}$.

Any semiconducting medium contains many types of localized flaw, of which we shall single out for examina-

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

[2] H. J. Bowlden, J. Phys. Chem. Solids **3**, 115 (1957).

[3] E. A. Milne, Phil. Mag. **47**, 209 (1924); L. H. Aller and D. H. Menzel, Astrophys. J. **102**, 239 (1945).

[4] N. Sclar and E. Burstein, Phys. Rev. **98**, 1757 (1955); E. Burstein *et al.*, in *Photoconductivity Conference*, edited by R. G. Breckenridge (John Wiley & Sons, Inc., New York, 1956), p. 353.

[5] P. T. Landsberg, in *Festkörperprobleme* (Vieweg, Braunschweig, Germany, 1967).

[6] Equations (1)–(3) and their ramifications are found in any standard semiconductor text, though the system of symbols varies. In some texts the statistical weight of a donor ground state (a number larger than unity) is written as β^{-1} so that one can write $f_d=\{1+\beta\exp[(-E_d-\phi)/kT]\}^{-1}$; see J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Inc., New York, 1962), p. 118.

tion a set of monovalent donors, density N_d per unit volume, with a ground-state binding energy E_d and a ground-state statistical weight[6] of g_d. Then the fraction of such donors for which the ground state is unoccupied can be written as

$$(1-f_d)=[1+g_d\exp((E_d+\phi_d)/kT)]^{-1}. \quad (3)$$

At equilibrium, ϕ_d coincides with ϕ, as $f_d\rightarrow f_{d0}$.

Away from thermal equilibrium, what we can say about rates of spontaneous and stimulated radiative transitions between these donors and the conduction band has to be tempered with our knowledge of the excited states of the donors, nonradiative mechanisms, other kinds of flaw, and the nature of the excitation. But none of these extraneous matters detracts from the statement that at equilibrium itself the rate of spontaneous radiative recombination from energy E in the conduction band to the donor ground states must equal the difference between the rates of photon-stimulated generation and recombination with respect to the same set of states:

$$\left(\frac{dr_{sp0}}{dE}\right)=\left[\left(\frac{dg_{st0}}{dE}\right)-\left(\frac{dr_{st0}}{dE}\right)\right]. \quad (4)$$

Such a statement is emphatically not generally true away from equilibrium, when the zeros are omitted from the subscripts.

It is appropriate to note here that Eq. (4) is correct at equilibrium whether or not the radiative transition is phonon-assisted. The definitions of σ_r and σ_i as in Eqs. (5) and (6) are particularly clear cut if there is no phonon involvement, but the treatment leading to Eq. (12) is not invalidated if some or all of the transitions are assisted. It must be remembered, though, that in the latter case σ_r and σ_i implicitly involve the phonon spectrum, and σ_i is liable to be appreciably temperature-dependent. (For a direct optical transition, σ_i will be affected by temperature only to the extent that lattice dilation modifies the electronic structure.)

The left side of Eq. (4) can be expressed as

$$(dr_{sp0}/dE)=f_{c0}(1-f_{d0})\sigma_r(E)v(E)N_d g(E), \quad (5)$$

where $\sigma_r(E)$ denotes the cross section presented by an ionized donor for spontaneous radiative capture of a free electron moving at speed $v(E)=(2E/m_c)^{1/2}$.

Following the van Roosbroeck–Shockley approach (and neglecting dispersion of the refractive index w), the rate of stimulated generation is

$$(dg_{st0}/dE)=f_{d0}(1-f_{c0})\sigma_i(h\nu)(N_d c/w)Q_{eq}(h\nu) \quad (6)$$

per unit volume per unit energy interval, where $\sigma_i(h\nu)$ is the photo-ionization cross section of a neutral donor to energy $E=(h\nu-E_d)$ in the conduction band, (c/w) is the speed of the interacting photons, and

$$Q_{eq}(h\nu)=\frac{8\pi(w/hc)^3(h\nu)^2}{\exp(h\nu/kT)-1} \quad (7)$$

is the Planck expression for the thermal density of photons (per unit volume per unit energy interval) of energy $h\nu=(E_d+E)$. Similarly, the stimulated downward rate is

$$(dr_{st0}/dE)=f_{c0}(1-f_{d0})\sigma_i(h\nu)(N_d c/w)Q_{eq}(h\nu), \quad (8)$$

so that

$$\left[\left(\frac{dg_{st0}}{dE}\right)-\left(\frac{dr_{st0}}{dE}\right)\right]=(f_{d0}-f_{c0})\sigma_i(h\nu)(N_d c/w)Q_{eq}(h\nu). \quad (9)$$

In Eq. (9), the quantity $[(f_{d0}-f_{c0})\sigma_i(h\nu)N_d]$ is just the contribution of the donors to the optical-absorption coefficient; we choose to express Eq. (9) in terms of a cross section rather than of an absorption coefficient in order to see more clearly what reciprocity means in the context of a single flaw.

Equation (4) requires that the right sides of Eqs. (5) and (9) be equal; utilizing Eqs. (1) and (7), the relationship of the two cross sections reduces to

$$\sigma_r(E)=\sigma_i(h\nu)\left[\frac{g_d w^2(h\nu)^2}{2c^2 m_c E}\right]\times\left\{\frac{f_{d0}-f_{c0}}{g_d f_{c0}(1-f_{d0})[\exp(h\nu/kT)-1]}\right\}. \quad (10)$$

The terms in the factor { } have been separated out because, as can be obtained using Eqs. (2) and (3),

$$\left\{\frac{f_{d0}-f_{c0}}{g_d f_{c0}(1-f_{d0})[\exp(h\nu/kT)-1]}\right\}=\left\{\frac{\exp(h\nu/kT)-(1/g_d)}{\exp(h\nu/kT)-1}\right\}, \quad (11)$$

which is exactly unity for a nondegenerate donor ground state, and will be essentially unity regardless of the ground-state degeneracy for temperatures appreciably smaller than $(h\nu/k)$. Then the less cumbersome statement

$$\sigma_r=\sigma_i\left[\frac{g_d w^2(h\nu)^2}{2c^2 m_c E}\right]=\sigma_i\left[\frac{g_d w^2(E_d+E)^2}{2c^2 m_c E}\right] \quad (12)$$

is valid under the conditions in which one is likely to be concerned with the result. Equation (12) corresponds with the result obtained by Milne[3] for the corresponding astrophysical problem, and further examined by Landsberg.[5]

III. RECIPROCITY AND THE UNCERTAINTY PRINCIPLE

Equation (12) has been obtained from statistical reasoning, considering the balance between the Bose distribution of photons and the Fermi distribution of electrons in a condition of thermodynamic equilibrium. The result itself holds good both at and away from equilibrium, and has a significance at the atomic level regardless of statistical significance.

Thus if we express Eq. (12) in the form

$$g_d^{1/2}(whv/c)\sigma_i^{1/2}=(2Em_c)^{1/2}\sigma_r^{1/2}, \tag{13}$$

it will be observed that the capture lengths of an interacting photon and an interacting electron are in inverse proportion to their respective momenta. This is an entirely natural consequence of the Heisenberg uncertainty principle.

The term "capture length" in the preceding paragraph is not synonymous with "localization length" for a photon or electron; thus each side of Eq. (13) can be considerably smaller than $\hbar$. For a hydrogen atom, in which[7] $\sigma_i\approx 0.23a_0^2$ for energies just at the Lyman continuum limit (here a_0 denotes the Bohr radius), then

$$g^{1/2}(hv_i/c)\sigma_i^{1/2}\approx(e^2/3c)=0.0024\hbar. \tag{14}$$

A much smaller value still will be found for transitions which are forbidden for any reason, characterized by very small oscillator strength.

The important thing to note is that the strength of coupling between a bound electron and the radiation field determines both the optical absorption and the ability of radiative recombination to compete with nonradiative processes. We can either measure absorption and compute recombination rates, or can observe efficient luminescence and compute the expected optical properties.

IV. THE THERMALLY AVERAGED CROSS SECTION

It will be seen from Eq. (12) that σ_r diverges for the minimum transition energy, when the states from which capture occurs are at the very bottom of the band.[8] There is no divergence, however, in the capture *rate* because of $E^{1/2}$ factors contributed by the electron speed $v(E)=(2E/m_c)^{1/2}$ and by the density of states $g(E)=4\pi E^{1/2}(2m_c/h^2)^{3/2}$ in integrating over the complete distribution. We shall define a *mean radiative capture cross section* $\bar{\sigma}_r$ by writing the total spontaneous radiative rate (from the band direct to the donor ground state) as

$$r_{sp}=nN_d(1-f_d)\bar{v}\bar{\sigma}_r. \tag{15}$$

Here

$$n=\int_0^\infty g(E)f_c(E)dE \tag{16}$$

is the total conduction-electron density, and

$$\bar{v}=\frac{1}{n}\int_0^\infty v(E)g(E)f_c(E)dE \tag{17}$$

is the mean electron speed. Then from Eq. (5), $\bar{\sigma}_r$ is integrally related to $\sigma_r(E)$ by

$$\bar{\sigma}_r=\left(\frac{1}{n\bar{v}}\right)\int_0^\infty v(E)\sigma_r(E)g(E)f_c(E)dE. \tag{18}$$

Equation (12) permits us to express $\bar{\sigma}_r$ as an integral with respect to the spectrally-dependent photo-ionization cross section:

$$\bar{\sigma}_r=\left(\frac{1}{n\bar{v}}\right)\left[\frac{8\pi g_d w^2}{h^3c^2}\right]\int_0^\infty (E_d+E)^2\sigma_i(hv)f_c(E)dE. \tag{19}$$

For many situations, Eq. (19) is more useful than Eq. (12). For whereas stimulated absorption can be measured as a function of E by conventional optical techniques, radiative recombination can often be measured only as a composite from all occupied states in the band.[9]

The literature on carrier capture by flaws seems about equally divided on the question of whether the capture rate averaged over a band should be quoted in terms of a capture cross section $\bar{\sigma}$ or of a capture coefficient $\bar{B}=(\bar{\sigma}\bar{v})$ or $(\bar{\sigma}v_{rms})$. As Lax[10] points out, any discrepancies in averaging procedures are not likely to involve systematic errors of more than a factor of $(v_{rms}/\bar{v})$ $[=(3\pi/8)^{1/2}$ for a Boltzmann distribution], quite unimportant when compared with the 10^{14}:1 range of possible rates of processes.

In order to make further progress beyond Eq. (19), it will be recalled that we suggested earlier in this paper that $f_c(E)$ be considered to be a Fermi factor both at, and away from, thermodynamic equilibrium. The integral in Eq. (19) simplifies when n is either very large or rather small. The asymptotic case of rather small total conduction-electron density (negative ϕ_c, Boltzmann distribution) is appropriate for consideration of spontaneous recombination. In this case if

$$f_c(E)\approx\exp[(\phi_c-E)/kT]\ll 1, \tag{20}$$

then

$$n=2(2\pi m_c kT/h^2)^{3/2}\exp(\phi_c/kT),$$
$$\bar{v}=(8kT/\pi m_c)^{1/2},$$

and when the conditions of Eq. (20) are applicable to

[7] D. H. Menzel and C. L. Pekeris, Mon. Not. Roy. Astr. Soc. **96**, 77 (1935).

[8] For a finite donor density, an upper bound on the increase of σ_r is set by the value of $N_d^{-2/3}$. However, this may typically be of the order of 10^{-12} cm^2, and would not represent a restriction except for free-carrier energies smaller than some 10^{-11} eV.

[9] If there is detectable recombination emission which can be measured as a function of $h\nu$, then of course Eq. (12) is immediately applicable.

[10] M. Lax, Phys. Rev. **119**, 1502 (1960).

Eq. (19), the mean capture cross section is

$$\bar{\sigma}_r=\left[\frac{g_d w^2}{2c^2 m_c (kT)^2}\right]\int_0^\infty (E_d+E)^2\sigma_i(h\nu) \times\exp(-E/kT)dE, \quad \phi_c<0. \quad (21)$$

It will be observed that this "thermally averaged" cross-section depends on temperature, but not on the conduction-electron density n (provided that the latter not be too large).

When the radiative transitions under consideration are phonon-aided, the temperature dependence of $\bar{\sigma}_r$ is determined at least in part by how σ_i varies with T. But even when σ_i is completely independent of temperature (as should be a reasonable approximation for a direct transition), there will be a characteristic variation of $\bar{\sigma}_r$ with T which is determined by how σ_i varies with $h\nu$ just above the threshold energy. If σ_i varies as $(h\nu-E_d)^m$ for transition energies just above threshold, then Eq. (21) dictates that $\bar{\sigma}_r$ will vary as $T^{(m-1)}$. Some examples of this are noted in the next section. The second and third of these (relating to indium in silicon) were discussed in a brief preliminary report of this work.[11]

V. EXAMPLES

A. Hydrogenic Donor Impurity

So frequently and so glibly do we speak of "hydrogenic" impurities in semiconductors that it comes as something of a shock to realize how rarely are all the conditions for hydrogenlike behavior likely to be satisfied. Obviously things are more complicated than a scaled hydrogenic model when the impurity is associated with two or more bands degenerate at the extremum, as happens for acceptors in semiconductors such as Ge, Si, or the III–V compounds. The ground states for group V donors in germanium or silicon are highly nonhydrogenic[12] because of the multi-ellipsoidal band structures; evidently we should look for an example of a spherically symmetric band extremum at the zone center, well removed in energy from any other extrema. The latter consideration rules out donors in semiconductors such as GaAs or GaSb, since subsidiary conduction band minima affect the form of the bound donor states.[13] Donors in InAs or InSb probably *are* hydrogenic in terms of their bound-state wave functions and eigenvalues, but n-type samples of these semiconductors always seem to have donor concentrations large enough to cause impurity banding, and an abolition of carrier freeze-out unless a considerable magnetic field is applied at low temperatures.[14]

The hopefully hydrogenic situation used as an example here is that of shallow donors in CdTe. Recent theoretical and experimental work[15] indicates that the conduction minium Γ_1 lies well below any other conduction minima, and Marple[16] deduces from Faraday effect that the isotropic effective mass associated with this minimum is $m_c=0.11m_0$. For a dielectric constant $w^2=K=10.6$, the ground-state binding energy of a hydrogenic donor should be

$$E_d=2\pi^2 m_c e^4/h^2 w^4=0.0133 \text{ eV}, \quad (22)$$

which agrees quite well with the value 0.010 eV deduced by Segall *et al.*[17] from the temperature dependence of electron density in CdTe samples containing $\sim 10^{15}$ cm^{-3} of shallow donors. Any influence of ionic binding would tend to push E_d beyond 0.0133 eV, as would departure from a strict Coulomb potential, and it seems that such tendencies must not be very important, since the measured ionization energy is a little smaller than the calculated hydrogenic one.[18]

For a strictly hydrogenic center, the photo-ionization cross section $\sigma_i(h\nu)$ rises as a step function at $h\nu=E_d$, and varies as $(E_d/h\nu)^3$ for energies not very much in excess of E_d:

$$\sigma_i(h\nu)=\left[\frac{w^3h^3}{8cm_c^2e^2}\right]\left(\frac{E_{\text{eff}}}{E_0}\right)^2\left(\frac{E_d}{h\nu}\right)^3, \quad 0\leqslant(h\nu-E_d)<E_d. \quad (23)$$

This behavior is displayed in Fig. 1. In Eq. (23), the factor $(E_{\text{eff}}/E_0)^2$ allows for the departure of the local field at the impurity from the macroscopic electromagnetic field; the correction is noted by Dexter[19] to be less severe than a strict Lorentz factor even for highly localized wave functions, and should be close to unity for a hydrogenic center in which the Bohr radius is much larger than the interatomic spacing. Equation (23) is analogous to the result quoted by Burstein *et al.*[4] for the specified energy range, and differs in scaled form from that quoted by Seaton[20] for hydrogen only in the fine details of the energy dependence. From Eqs. (12), (22), and (23) the radiative recombination cross section is

[11] J. S. Blakemore, Bull. Am. Phys. Soc. **12**, 356 (1967).

[12] This is well demonstrated for silicon donors by W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

[13] As with sulphur donors in GaSb; see B. B. Kosicki, W. Paul, A. J. Strauss, and G. W. Iseler, Phys. Rev. Letters **17**, 1175 (1966).

[14] M. A. C. S. Brown and M. F. Kimmitt, Infrared Phys. **5**, 93 (1965).

[15] J. L. Shay, W. E. Spicer, and F. Herman, Phys. Rev. Letters **18**, 649 (1967).

[16] D. T. F. Marple, Phys. Rev. **129**, 2466 (1963).

[17] B. Segall, M. R. Lorenz, and R. E. Halsted, Phys. Rev. **129**, 2471 (1963).

[18] Since the average interimpurity spacing is only about 19 times the "Bohr radius" of 51 Å for 10^{15} donors per cm^3, some reduction of the measured ionization energy compared with that for infinite donor dilution is to be expected. Any large deviation from hydrogenic behavior would result in a much larger *upwards* shift of the ionization energy.

[19] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 355.

[20] M. J. Seaton, Rept. Progr. Phys. **23**, 313 (1960).

(assuming that $g_d=2$ and that $E_{\text{eff}}\approx E_0$)

$$\sigma_r(E)=\left[\frac{\pi^2 whe^2}{4c^3m_c^2}\right]\frac{E_d^2}{E(E+E_d)}, \quad (24)$$

of which the dependence on E^{-1} will be much more important than the dependence on $(E+E_d)^{-1}$ in determining the Boltzmann-averaged value if $(E_d/kT)\gg 1$. This averaged value, by the procedures of Eqs. (18) and (19), is

$$\bar{\sigma}_r=[\pi^4e^6/2c^3w^3hm_ckT]=7.0\times10^{-18}T^{-1}\text{ cm}^2 \quad (25)$$

for a supposedly hydrogenic donor in CdTe. Note that in accordance with the previously cited rule relating energy dependence of $\sigma_i(h\nu)$ to temperature of $\bar{\sigma}_r$, the lack of explicit dependence of σ_i in Eq. (23) on $(h\nu-E_d)$ leads to a T^{-1} dependence for $\bar{\sigma}_r$ in Eq. (25).

The radiative cross section of Eq. (25) is very small compared with the likely strength of phonon cascade recombination[10] for a hydrogenlike center at low temperatures, thus the magnitude and temperature dependence of recombination from the conduction band of a semiconductor such as CdTe to shallow donors may be quite different from the predictions of Eq. (25).

B. Indium Acceptor in Silicon

For recombination from the valence band of silicon to indium acceptors, the total rate of recombination is also determined in practice by phonon-emission processes rather than by direct photon emission. It is chosen as another example for study because the spectral characteristics of σ_i (and hence the temperature characteristics of $\bar{\sigma}_r$) are quite different from the hydrogenic impurity example discussed above.

The ground-state binding energy exceeds the hydrogenic value for all group III acceptors in silicon, but the value for indium ($E_a=0.155$ eV) is much larger than for the lighter members of the group III family.[4] The excited "p-like" states are rather similar for the various acceptors, and have energies not far from the expectations of an effective-mass model,[21] but the "1s" ground state is particularly sensitive to the form of the potential close to the impurity site, which for indium (an atom considerably larger than silicon) evidently departs from a Coulomb potential.

Two attempts have recently been made to describe the ground-state wave function for an indium acceptor, each generating an expression for the photo-ionization cross section which may be compared with the experimentally determined cross section.[4,22] In one of these studies, Bebb[23] has approached indium acceptors from the standpoint of the quantum-defect method. In the other, Lucovsky[24] has assumed that the ground state is

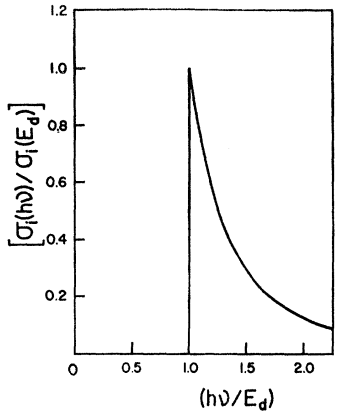

FIG. 1. Spectral dependence of the photo-ionization cross section for an impurity in a semiconductor which is strictly hydrogenic in its properties [Eq. (23)].

similar to that for a square-well potential of amplitude adjusted to give the experimentally observed ionization energy. The ground-state wave function is then a suitably normalized form of that for the ground state of the deuteron, and the photo-ionization cross section is calculated just as for the corresponding deuteron problem (given in any elementary nuclear physics text). Following Lucovsky, we can express the ionization cross section as

$$\sigma_i(h\nu)=\left[\frac{w^3h^3}{8cm_v^2e^2}\right]\left(\frac{E_{\text{eff}}}{E_0}\right)^2 \times\left[\frac{(h\nu-E_a)^{3/2}E_a^{1/2}E_H}{(h\nu)^3}\right], \quad h\nu\gtrsim E_a, \quad (26)$$

where E_a denotes the actual binding energy of the ground state, and E_H is the binding energy for a hydrogenic state.

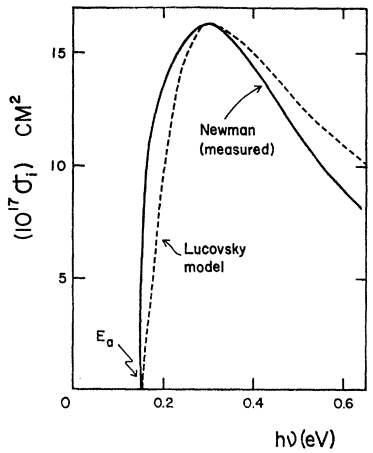

FIG. 2. Photo-ionization cross section as a function of photon energy for a neutral indium acceptor in silicon. Comparison of the measured cross section (Newman, Ref. 22) with the Lucovsky model, Eq. (26), for $E_a=0.155$ eV, $m_v=0.53m_0$, $w=3.4$, and $E_{\text{eff}}=2.1E_0$.

[21] D. Schechter, J. Phys. Chem. Solids **23**, 237 (1962).
[22] R. Newman, Phys. Rev. **99**, 465 (1955).
[23] H. B. Bebb, Bull. Am. Phys. Soc. **12**, 342 (1967).
[24] G. Lucovsky, Solid State Commun. **3**, 299 (1965).

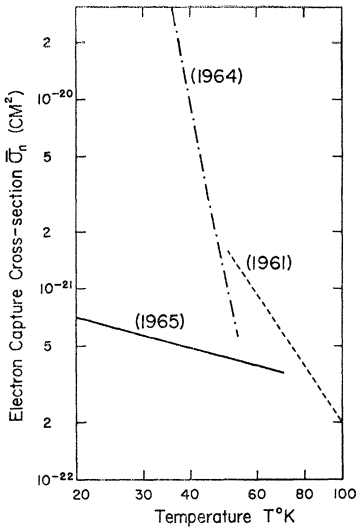

FIG. 3. Electron-capture cross section exhibited by neutral indium centers in silicon as a function of temperature, from the reports of Pokrovsky and Svistunova. It is likely that their data of 1961 (Ref. 29) and 1964 (Ref. 30) was affected by donor-acceptor transitions, and efforts were made to avoid this in taking the 1965 data (Ref. 31).

In contrast with the hydrogenic expression of Eq. (23), the cross section of Eq. (26) has its maximum value when $h\nu=2E_a$, rising as the $\frac{3}{2}$ power of the free-hole kinetic energy just above threshold. Figure 2 compares the experimentally determined photo-ionization curve of Newman[22] with Eq. (26), chosen to coincide at the peak by letting $(E_{\text{eff}}/E_0)=2.1$. It can be seen that the theoretical result of this very simple model accounts rather well for the experimentally observed form with indium acceptors, and the magnitude of the required local-field correction is entirely reasonable.[25] Recent measurements of the photo-ionization curve near threshold[26] do not entirely confirm Newman's curve, and agree much more closely with the curve of Lucovsky's simple theoretical model.

The detailed balance arguments of Eq. (12) can be used to express the radiative recombination cross section $\sigma_r(E)$ corresponding with the $\sigma_i(h\nu)$ of Eq. (26). In turn, Eq. (21) can be used to determine the thermally averaged radiative-recombination cross section $\bar{\sigma}_r$. In accordance with the previous notation that a variation of σ_i as $(h\nu-E_a)^m$ will result in $\bar{\sigma}_r$ varying as T^{m-1}, for indium centers the radiative cross section must vary as $T^{1/2}$. If we assume that $(E_{\text{eff}}/E_0)=2.1$, and that the acceptor ground state is sixfold degenerate,[27] then Eqs. (21) and (26) yield

$$\bar{\sigma}_r=8.3\times10^{-22}T^{1/2}\ \text{cm}^2. \tag{27}$$

[25] The quantum-defect approach (Ref. 23) also works quite well for indium, and has the additional merit that it is successful also in the treatment of the more shallow acceptors.

[26] C. E. Sarver and J. S. Blakemore (to be published).

[27] The degeneracy of the indium ground state in silicon should be taken as equal to six because the binding energy is much larger than the spin-orbit splitting energy: see D. Schechter, Ref. 21.

The *total* recombination cross section for holes in silicon presented by indium acceptors is larger than that of Eq. (27) by some seven orders of magnitude[28] and has a temperature dependence dictated by the dominant phonon-emission processes. This disparity reminds us that radiative processes are likely to be dominant only when the opportunities for phonon cascade or multiphonon processes are absent. The next example is of a likely contender for this role.

C. Electron Capture by Indium Acceptors in Silicon

Ionized indium acceptors in silicon are very efficient at capturing free holes, but the capture of free *electrons* by *neutral* indium acceptors is a much slower process. Such capture has been studied by Pokrovsky and Svistunova,[29–31] who report by photon counting methods that free-electron recombination to neutral indium atoms is almost completely radiative. They have used transient photoconductive decay methods in measuring extrinsic lifetimes (and hence attempting to deduce the temperature dependence of the thermally averaged electron-capture cross section) with results as shown in Fig. 3. Apparently the time constants in their earlier work were affected by donor-acceptor recombination,[32] and attempts were made to exclude this in securing the results of Ref. 31. This most recent curve in Fig. 3 fits

$$\bar{\sigma}_n=3\times10^{-21}T^{-1/2}\ \text{cm}^2. \tag{28}$$

Now if the recombination is indeed totally radiative, we can use Eq. (28) to determine the spectral dependence and magnitude of the photo-ionization cross section just above threshold. From the arguments of Sec. IV, the $T^{-1/2}$ dependence of $\bar{\sigma}_n$ requires $\sigma_i(h\nu)$ to vary as the square root of the electronic kinetic energy $(h\nu+E_a-E_i)$ just above the threshold at $h\nu_0=(E_i-E_a)$. Applying Eq. (21) to Eq. (28), the excitation of electrons from *ionized* indium acceptors into conduction band states must follow

$$\sigma_i(h\nu)=1.5\times10^{-17}(h\nu+E_a-E_i)^{1/2}\ \text{cm}^2 \tag{29}$$

for the first few tens of millielectron volts above threshold.

At this point it is tempting to compare Eq. (29) with the results of the theoretical models of Eagles[33] and of Dumke[34] for radiative transitions between a hydrogenic

[28] J. S. Blakemore, Can. J. Phys. **34**, 938 (1956); E. E. Godik and Y. E. Pokrovsky, Fiz. Tver. Telad [English transl.: Soviet Phys.—Solid State **6**, 1870 (1965)].

[29] Y. E. Pokrovsky and K. I. Svistunova, J. Phys. Chem. Solids **22**, 39 (1961).

[30] Y. E. Pokrovsky and K. I. Svistunova, Fiz. Tver. Telad [English transl.: Soviet Phys.—Solid State **5**, 1373 (1964)].

[31] Y. E. Pokrovsky and K. I. Svistunova, Fiz. Tver. Telad [English transl.: Soviet Phys.—Solid State **7**, 1478 (1965)].

[32] A. Honig and R. Enck, *Radiative Recombination Symposium*, edited by C. Benoit (Dunod Cie., Paris, 1964), p. 113.

[33] D. M. Eagles, J. Phys. Chem. Solids **16**, 76 (1960).

[34] W. P. Dumke, Phys. Rev. **132**, 1998 (1963).

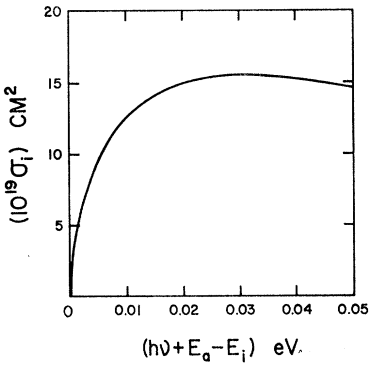

FIG. 4. Anticipated photo-ionization curve for electrons from ionized indium acceptors to conduction-band levels in silicon, based on comparison with the Eagles-Dumke model (Refs. 33, 34) with magnitude dictated by the strength of supposedly radiative recombination [Eq. (28)].

acceptor and the conduction band in a direct-gap semiconductor. The ways in which silicon as host and indium as acceptor fail to meet the initial assumptions of the model are obvious, but it is intriguing that an initial rise of $\sigma_i(h\nu)$ similar to that of Eq. (29) is predicted. The Eagles-Dumke models predict

$$\sigma_i(h\nu)=\sigma_{\max}\left\{\frac{9[(h\nu+E_a-E_i)/E_a(m_v/m_c)]^{1/2}}{2[1+(h\nu+E_a-E_i)/E_a(m_v/m_c)]^4}\right\} \quad (30)$$

as the spectral dependence of a potentially measurable optical-absorption process in the range $(E_i-E_a)\leqslant h\nu \leqslant E_i$. The maximum cross section is reached when $(h\nu+E_a-E_i)\approx(E_a m_v/7m_c)$, and the numerator will dominate the energy dependence for appreciably smaller values of electronic kinetic energy. In order that Eq. (29) should be interpreted as the beginning of a curve whose wider range spectral dependence is given by Eq. (30), we must set $\sigma_{\max}=1.56\times10^{-18}$ cm^2 at a photon energy 0.03 eV above threshold. The corresponding complete photo-ionization curve is shown in Fig. 4.

It is immediately apparent from Fig. 4 that this is a very weak process to measure by standard optical techniques, for a sample 0.5 cm thick containing 10^{16} cm^{-3} of ionized indium acceptors would absorb less than 1% of incident radiation by this photo-ionization process (at the energy of the "peak" absorption). Staflin[35] has reported an apparent small increase in absorption of an indium-doped-silicon sample at room temperature above a threshold photon energy of 0.97 eV, using phase-sensitive methods to attempt separation of any small photo-ionization absorption from the immensely larger amount of free-hole absorption. Staflin did not reduce his data to a quantitative form, and since he reported the rise in absorption above 0.97 eV only for a single sample, it would seem that conclusive verification of the photo-ionization curve postulated by Fig. 4 is lacking at this point. Experiments are planned in the hope of resolving this question.

Before adjourning discussion of the capture of electrons in silicon by neutral indium acceptors (and of the reciprocal process), it should be noted that Pokrovsky and Svistunova's assessment of the capture cross section is in conflict with the results of some other experiments. Wertheim[36] reported some years ago a much larger cross section ($\bar{\sigma}_n\sim10^{-17}$ cm^2) using data on the transient decay following intrinsic excitation, a technique which admittedly does have possible complications. More recently, however, cross sections in the range 10^{-18}–10^{-16} cm^2 have been deduced from space-charge-limited current experiments[37] and similar studies[38] with semi-insulating indium-doped silicon. A universal model which permits one to account for the results of all types of measurements on indium-doped silicon does not appear to be immediately at hand.

[35] T. Staflin, J. Phys. Chem. Solids **26**, 563 (1965).
[36] G. K. Wertheim, Phys. Rev. **109**, 1086 (1958).
[37] J. L. Wagener and A. G. Milnes, Solid-State Electron. **8**, 495 (1965).
[38] J. S. Barrera, Ph.D. thesis, Carnegie Insititute of Technology, 1966 (unpublished).