Ham calculates that an anisotropy in $\mathbf{k}_F$ of about 1% would lead to an anisotropy in the cyclotron mass of about 6%. From our experimental data we would place an upper limit of 2% on the anisotropy of the cyclotron mass in potassium. Thus it appears that the anisotropy in $\mathbf{k}_F$ is appreciably less than 1% for potassium. Knowing that the Fermi surface of potassium is essentially spherical, we can use the extremal cross-sectional area obtained from de Haas–van Alphen data[24] to calculate the radius of the Fermi surface, $k_F = 7.44 \pm 0.07 \times 10^7$ cm^{-1}, and then we can use the measured cyclotron mass to obtain the Fermi velocity $v_F = 7.1 \pm 0.2 \times 10^7$ cm/sec. It may well be that these two numbers provide a more detailed knowledge of the electronic structure of potassium than is known for any other metal!

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Optical Transitions Involving Impurities in Semiconductors*

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The theory of optical transitions between donor levels and the valence band or between acceptor levels and the conduction band has been examined. Expressions for the optical absorption and radiative lifetime due to such transitions are derived. Application of this theory is made to GaAs and it is shown that at relatively high impurity concentrations optical transitions involving impurities can give rise to moderately high absorption constants and short radiative lifetimes. In the intermetallic semiconductors which have a conduction band effective mass much smaller than that of the valence band, the transition probability between acceptor states and the conduction band may be taken to be a constant up to moderate conduction band energies. To test the limits of validity of band to impurity recombination, the minimum spontaneous radiative lifetimes for electrons and holes are calculated. For electrons in GaAs this minimum lifetime is 0.3 nsec.

INTRODUCTION

In the past several years much attention has been focused on interband transitions in both the optical emission and absorption spectrum of semiconductors. Analysis of such data has yielded information concerning both the band structure and scattering mechanisms in many substances.

More recently, light emitting diodes of GaAs with a high quantum efficiency have been studied by many workers,[1,2] and stimulated emission from such diodes has been observed[3–5] at high current densities. The light emitted from these diodes is at an energy slightly below the energy band gap, and as a result does not suffer the intense reabsorption which would occur for photons emitted above the direct transition edge. Nathan and Burns[6] have noted the similarity between the emission from GaAs diodes and photoluminescence from Zn-doped GaAs, and it seems that the acceptors are involved in the light emission even though in the more highly doped diodes the acceptor levels would probably not be either localized or discrete in energy.

We have studied transitions between impurities and energy bands in order to discover how important the absorption and recombination given rise to by such transitions might be in a substance such as GaAs. We have found that impurities, particularly acceptors, furnish not only a transition which is below the normal absorption edge, but that transitions to acceptors can provide a strong radiative recombination mechanism able to compete effectively with other recombination mechanisms.

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[*] A brief account of this work was presented at the American Physical Society St. Louis Meeting, March, 1963. [Bull. Am. Phys. Soc. **8**, 201 (1963)].

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Transitions between acceptor levels and the conduction band had previously been studied by D. M. Eagles[7] in a qualitatively successful attempt to explain an apparent shift of the band edge to longer wavelengths in p-type GaAs when compared to n-type GaAs. Eagles derived the absorption spectrum and the form of the emission spectrum assuming simple energy bands. An accurate fit of the absorption or emission spectra did not appear to be possible due to the spread in energy of the acceptor levels.

In this work we have used many of the same assumptions employed by Eagles. In our formulation, however, the impurities are not assumed to have an energy given by the hydrogenic approximation and the effects of multiple valence bands are explicitly taken into account. In addition, the absorption and the lifetimes for spontaneous radiative recombination are evaluated using the known parameters of semiconductors such as GaAs. This is done for donor-valence band transitions, as well as for acceptor-conduction band transitions.

Finally, partly to test the limits of applicability of band to impurity transitions, and partly to see how short radiative lifetimes can be in semiconductors, we have calculated the minimum possible spontaneous radiative lifetimes for electrons and holes.

TRANSITION PROBABILITY

The model upon which our calculations are based incorporates the following assumptions: (1) a direct energy band gap; (2) discrete, shallow, nonoverlapping impurity states; (3) a slowly varying hydrogenic envelope function for the impurity (the special extent of which is given by the impurity binding energy); (4) a valence or conduction band density of states unaffected by the presence of many impurities. In addition, we will limit our considerations to the ground state of the impurity.

We will consider first the donor-valence band transition, keeping in mind that our treatment applies equally well to the acceptor-conduction band transition with a few changes in notation. If any differences in treatment are necessary due to the valence band degeneracy, these will be taken into account and final expressions for observable quantities will be given for both types of transitions.

The valence band wave functions are the usual Bloch states given by $\psi_{v\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{v\mathbf{k}}(\mathbf{r})$, where $\mathbf{k}$ is the wave vector of the electron and $u_{v\mathbf{k}}(\mathbf{r})$ the cell periodic part of $\psi_{v\mathbf{k}}$, which is normalized in a crystal of unit volume. The transition rate between valence band states and N_D randomly centered but not overlapping bound donor states is N_D times the transition rate to a single donor, so that it is only necessary to consider one donor. The donor wave functions are given in the usual effective mass approximation as[8]

$$\psi_D=(1/\pi^{1/2}a_D^{3/2})e^{-r/a_D}u_{c0}(\mathbf{r}). \tag{1}$$

Here

$$a_D=(\epsilon\hbar^2/ze^2m_c)=(ze^2/2\epsilon E_D), \tag{2a}$$

where ze is the charge of the ionized donor, ϵ the dielectric constant, E_D the donor binding energy, and m_c the conduction band effective mass. For acceptors, the ground state is somewhat more complicated because of the degenerate valence band structure which usually seems to occur. We shall define an equivalent simple effective mass m_A, and also an acceptor orbit radius a_A in terms of the acceptor binding energy E_A, in order to conveniently describe the spatial extent of the acceptor wave function.

$$a_A=(\epsilon\hbar^2/ze^2m_A)=(ze^2/2\epsilon E_A). \tag{2b}$$

The optical transition probability may be calculated using the interaction Hamiltonian $H'=-(eA/\mathrm{mc})\hat{a}\cdot\mathbf{P}$, where $A\hat{a}$ is the vector potential of the electromagnetic field and $\mathbf{P}=(\hbar/i)\nabla$ is the momentum operator for electrons.

The matrix elements of H' will be taken between the combined states of the electrons and of the electromagnetic field. The allowed matrix elements for transitions between valence band and donor states, induced by a mode with N photons, are given by[9]

$$H'_{D,v\mathbf{k}}=-(e/\mathrm{nm})(2\pi\hbar N/\omega)^{1/2}\mathbf{P}_{D,v\mathbf{k}}\cdot\hat{a} \tag{3a}$$

for photon absorption, and

$$H'_{D,v\mathbf{k}}=-(e/\mathrm{nm})[2\pi\hbar(N+1)/\omega]^{1/2}\mathbf{P}_{D,v\mathbf{k}}\cdot\hat{a} \tag{3b}$$

for photon emission. Here n is the index of refraction. Assuming that the donor envelope wave function is slowly varying compared to u_{c0} we find that

$$\begin{aligned}
\mathbf{P}_{v\mathbf{k},D}&=\int e^{-i\mathbf{k}\cdot\mathbf{r}}u_{v\mathbf{k}}^*\mathbf{P}\psi_D d\mathbf{r}\\
&=\frac{\mathbf{P}_{vc}}{\pi^{1/2}a_D^{3/2}}\int e^{-(i\mathbf{k}\cdot\mathbf{r}+r/a_D)}d\mathbf{r},\\
\mathbf{P}_{v\mathbf{k},D}&=\frac{8\pi^{1/2}\mathbf{P}_{vc}}{a_D^{3/2}(1/a_D^2+\mathbf{k}^2)^2}\\
&=\frac{2^{9/4}\pi^{1/2}\hbar^{3/2}\mathbf{P}_{vc}}{(m_cE_D)^{3/4}[1+(m_v/m_c)(E_{v\mathbf{k}}/E_D)]^2},
\end{aligned} \tag{4}$$

where $E_{v\mathbf{k}}=\hbar^2k^2/2m_v$ is the kinetic energy of a hole of wave number $\mathbf{k}$ in the valence band. In the case where there are multiple valence bands, we must consider the transitions due to each band.

The optical transition probability per unit time for a transition between a valence band state and a donor

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[7] D. M. Eagles, Phys. Chem. Solids 16, 76 (1960).

[8] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 274.

level, induced by the interaction of one electromagnetic mode, is given in terms of the above matrix elements by the standard expression of time-dependent perturbation theory[9] as

$$\mathcal{P}_{v\mathbf{k},D}=(2\pi/\hbar)|H'_{D,v\mathbf{k}}|^2\delta(\hbar\omega+E_D-E_G-E_{v\mathbf{k}}), \quad (5)$$

or substituting from expressions (2)–(4)

$$\mathcal{P}_{v\mathbf{k}}=\frac{64\sqrt{2}\pi^3e^2\hbar^4|P_{vc}|^2{}_{\text{av}}\delta(\hbar\omega+E_D-E_G-E_{v\mathbf{k}})}{n^2m^2\hbar\omega(m_cE_D)^{3/2}[1+(m_vE_{v\mathbf{k}}/m_cE_D)]^4} \times\begin{cases}N, \text{ absorption}\\ N+1, \text{ emission}\end{cases}, \quad (6)$$

where P_{vc}, the interband matrix element of the momentum operator, is averaged over possible polarizations of the electromagnetic mode.

The corresponding expression for the acceptor-conduction band transition is modified by the factor $(m_AE_A)^{3/2}[1+(m_cE_{c\mathbf{k}}/m_AE_A)]^4$ in the denominator.

Two features of the transition probability should be noted. For transitions involving energy band states of very small **k**, the transition probability is proportional to $(m_cE_D)^{-3/2}\sim E_D^{-3}$ for donors, or $(m_AE_A)^{-3/2}\sim E_A^{-3}$ for acceptors, since a more spread out impurity state will have Fourier components of larger amplitude for small **k**. However, as **k** (and consequently the kinetic energy $E_{v\mathbf{k}}$ or $E_{c\mathbf{k}}$ of the energy band state) increases, the transition probability rapidly becomes smaller. If we consider transitions between a heavy mass valence band and donor states this decrease occurs at a very small energy of order $E_{v\mathbf{k}}\approx(m_c/m_v)E_D$. Typical values of m_c/m_v are between 0.2 and 0.1 in intermetallic semiconductors and E_D is typically less than 0.01 eV. For the case of transitions between acceptors and a simple conduction band, the decrease in the transition probability occurs at $E_{c\mathbf{k}}\approx(m_A/m_c)E_A$, but since the ratio m_A/m_c is typically 5 to 10 and since the acceptor binding energies are of order 0.01–0.10 eV the transition probability can be essentially constant over those conduction band energies normally occupied by electrons.

OPTICAL ABSORPTION

The absorption constant may be calculated using the relationship which relates the spatial and time rates of decay of the photon population,

$$K=(n/c)(1/N)(dN/dt). \quad (7)$$

To obtain dN/dt, we must sum the transition probability over all initial valence band states, and over the final states of unoccupied donors. Assuming a donor ground state degeneracy of two (spin up or down), we obtain for the absorption constant

$$K=\frac{256\pi e^2\hbar|P_{vc}|^2{}_{\text{av}}E_v{}^{1/2}}{ncm^2\hbar\omega(m_cE_D)^{3/2}} \times\sum_v\frac{m_v{}^{3/2}}{[1+(m_vE_v/m_cE_D)]^4}(N_D-n_D), \quad (8)$$

where $E_v=(\hbar\omega+E_D-E_G)$ corresponds to the kinetic energy in the valence band, and (N_D-n_D) is the number of unfilled donors. The sum over the light and heavy hole valence bands includes each type of band once, since the twofold time reversal degeneracy has already been taken account in the density of states. The expression for the absorption due to acceptor-conduction band transitions, taking four for the degeneracy of the acceptor level is

$$K=\frac{512\pi e^2\hbar|P_{vc}|^2{}_{\text{av}}E_c{}^{1/2}m_v{}^{3/2}}{ncm^2\hbar\omega(m_AE_A)^{3/2}[1+(m_cE_c/m_AE_A)]^4}(N_A-p_A), \quad (9)$$

where $E_c=(\hbar\omega+E_A-E_G)$, and (N_A-p_A) is the number of unfilled (with holes) acceptors.

In order to evaluate K, we must know the value of $|P_{vc}|^2{}_{\text{av}}$. This may be obtained from a knowledge of the conduction band effective mass, assuming a $\mathbf{k}\cdot\mathbf{P}$ interaction between only the valence and lowest conduction bands.[10] We may then proceed using the method of either Kane[11] or Dresselhaus,[12] assuming that both warping and linear spin orbit effects are unimportant.

From the valence band wave functions one can show that

$$|P_{lc}|^2{}_{\text{av}}=|P_{hc}|^2{}_{\text{av}}=|P_{sc}|^2=\tfrac{1}{2}|P_{\mathbf{k}lc}|^2, \quad (10)$$

where l, h, and s refer to the light, heavy, and split of valence bands.

We may write the "f sum rule"[13] for the conduction band mass as

$$(m/m_c)-1=(2/m)|P_{\mathbf{k}lc}|^2[(2/E_G)+(1/E_G+\Delta E)], \quad (11)$$

where ΔE is the spin orbit splitting of the valence bands at $\mathbf{k}=0$. For GaAs, with $m_c=0.072m$,[14] $E_G=1.51$ eV and $\Delta E=0.35$ eV, we obtain $|P_{vc}|^2{}_{\text{av}}=1.15$ m E_G. It should be emphasized that this is the average of the matrix element squared between only one of the conduction bands and one of the twofold degenerate light or heavy hole bands.

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[9] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, London, 1944), 2nd ed., p. 59.

[10] The square of the momentum matrix element may also be obtained from an analysis of the interband absorption data. The value so obtained for GaAs is approximately 30% larger than the value calculated from the conduction band effective mass.

[11] E. O. Kane, Phys. Chem. Solids **1**, 249 (1957).

[12] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).

[13] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1953), 2nd ed.

[14] E. D. Palik, J. R. Stevenson, and R. F. Wallis, Phys. Rev. **124**, 701 (1961).

Evaluating expression (9) for the absorption due to $10^{17}/\text{cm}^3$ compensated or ionized zinc acceptors in GaAs, with $E_A = 0.04$ eV and $\epsilon = 12.6$ ($m_A = 0.47$ m), at $E_c = \hbar\omega + E_A - E_G = 0.02$ eV, we find that $K = 300\ \text{cm}^{-1}$. This is in rough agreement with values of the absorption observed in the sharply rising edge of Zn-doped GaAs, but a more quantitative comparison is not possible because (1) the degree of compensation is usually not known, and (2) the high doping tends to smear out any structure.

We shall not discuss the optical emission spectrum, since the shape of the emission line rather than its absolute intensity is usually of interest, and Eagles[7] has discussed this at length. In addition, the width of the emission lines for transitions involving impurities are considerably broader than theory would predict (possibly due to a distribution in energy of impurity levels), and therefore a theoretical fit of the emission line shape does not appear to be possible.

RADIATIVE LIFETIMES

The lifetime for spontaneous radiative recombination may be obtained for a given carrier distribution if we sum over all the radiative transition which may occur. We will first sum over the electromagnetic modes whose density of states (per unit volume) is $\rho(\hbar\omega) = (n^3\omega^2/\pi^2\hbar c^3)$. We define

$$\mathcal{R}_{v\mathbf{k},D} = \int \mathcal{P}_{v\mathbf{k},D}\,\rho(\hbar\omega)\,d(\hbar\omega)\,, \tag{12}$$

which corresponds to the probability per unit time for radiative recombination of an electron in a single donor and a hole in the state labeled $v\mathbf{k}$. The recombination rate (in which we will ignore any generation due to the backbody background) is given by

$$-dp/dt = p/\tau_p = n_D \int_0^\infty f_p(E_v)\,\mathcal{R}_{v\mathbf{k},D}\,\rho(E_v)\,dE_v\,, \tag{13}$$

where n_D is the number of electrons in donors per unit volume, τ_p the hole lifetime, the distribution function for holes is

$$f_p(E_v) = p[2\exp(-E_v/kT)/\sqrt{\pi}g(kT)^{3/2}]\,,$$

and g is defined in terms of the density of valence band states by $\rho(E_v) = gE_v^{1/2}$.

First consider the lifetimes of carriers at $\mathbf{k}=0$, where the recombination probability is a maximum. For holes at $\mathbf{k}=0$ recombining with n_D bound electrons the lifetime is given by

$$\frac{1}{\tau_{p0}} = n_D\mathcal{R}_{v0,D} = 64\sqrt{2}\pi n \frac{e^2\hbar^2\omega|P_{vc}|^2_{\text{av}}}{c^3m^2(m_cE_D)^{3/2}}\,n_D\,, \tag{14}$$

and the lifetime for electrons at $\mathbf{k}=0$ recombining with p_A bound holes by

$$\frac{1}{\tau_{n0}} = p_A\mathcal{R}_{c0,A} = 64\sqrt{2}\pi n \frac{e^2\hbar^2\omega|P_{vc}|^2_{\text{av}}}{c^3m^2(m_AE_A)^{3/2}}\,p_A\,. \tag{15}$$

TABLE I. Numerically calculated values of the function $\Gamma(\alpha)$ [see Eq. (16)] for selected values of α.

α	$\Gamma(\alpha)$	α	$\Gamma(\alpha)$
100	0.94	3	0.31
50	0.89	2	0.23
30	0.83	1.4	0.17
20	0.77	1	0.12
14	0.70	0.7	0.080
10	0.61	0.5	0.053
7	0.52	0.35	0.034
5	0.43	0.2	0.017

More generally, these lifetimes will be increased due to the smaller transition probability for carriers of higher energy. For the case of electrons recombining from a Boltzmann distribution,

$$1/\tau_n = (1/\tau_{n0})\Gamma(T)\,,$$

where

$$\Gamma(T) = \frac{2}{\sqrt{\pi}(kT)^{3/2}} \int_0^\infty \frac{e^{-E_c/kT}E_c^{1/2}dE_c}{[1+(m_cE_c/m_AE_A)]^4}\,. \tag{16}$$

Changing variables to $y = m_cE_c/m_AE_A$, and introducing $\alpha = m_AE_A/m_ckT$,

$$\Gamma(\alpha) = \frac{2}{\sqrt{\pi}}\alpha^{3/2} \int_0^\infty \frac{e^{-\alpha y}y^{1/2}dy}{(1+y)^4}\,. \tag{17}$$

α is a measure of the extent to which the electrons are concentrated in states of small $\mathbf{k}$ values, where the recombination probability is highest. In Table I we present values of $\Gamma(\alpha)$ numerically calculated for various values of α.

The expression for Γ at large α is

$$\Gamma(\alpha) = 1 - 6/\alpha + 75/2\alpha^2 - 525/2\alpha^3 \cdots.$$

Because of impurity ionization at temperatures when $kT \sim E_A$ or E_D, the limit for small α is of little importance.

Similarly, for the case of hole recombination with bound electrons, $1/\tau_p = 1/\tau_{p0}\Gamma$. However, Γ is slightly more complicated due to the presence of both light and heavy holes. For this case,

$$\Gamma = \sum_v \frac{g_v}{g}\Gamma(\alpha_v)\,, \quad v = l,\ h\,, \tag{18}$$

where $\alpha_v = (m_DE_D/m_vkT)$ and $g_v/g = m_v^{3/2}/m_l^{3/2} + m_h^{3/2}$. The factor g_v/g simply weights the recombination according to the fraction of holes in the light or heavy hole band.

Let us take the above expressions for carrier lifetimes and apply them to the recombination of electrons and holes in GaAs. First consider electrons recombining with acceptors of binding energy 0.04 eV at 77°K. Taking $\epsilon=12.6$ we calculate that $m_A=0.47$ m. Evaluating Eq. (15) for $\alpha=40$ or $\Gamma=0.86$, we find that $1/\tau_n=0.43\times10^{-9}p_A$ sec^{-1} cm^3. For 10^{18} cm^{-3} bound holes the electron lifetime at 77°K is therefore 2.3 nsec.

For the case of holes recombining with electrons in hydrogenic donor states with $E_D=0.0062$ eV at 20°K we assume that $m_h=0.5$ m and $m_l=0.12$ m corresponding to $\Gamma(\alpha_h)=0.055$ and $\Gamma(\alpha_l)=0.24$. We can see that a light hole at 20°K is more than four times more likely to recombine with a bound electron than is a heavy hole, reflecting the lower average **k** values of the light holes. Substituting into the expression for the reciprocal hole lifetime we find that $1/\tau_p=0.8\times10^{-8}n_D$ cm^3 sec^{-1}. Although approximately only 10% of the holes are in the light hole band they contribute 34% of the recombination. For $n_D=5\times10^{15}$ the hole lifetime $\tau_p=2.5\times10^{-8}$ sec.

LIMITS OF VALIDITY

Although the inverse lifetimes that we have calculated are proportional to the impurity concentrations, it is clear that we cannot continue to shorten the lifetime by increasing the impurity concentration to arbitrarily high values. At high concentrations significant overlap between the wave functions of adjacent impurities will modify the wave function of the impurities so that the above theory will not be applicable. However, with a small amount of overlap of the impurity states, the impurity wave functions will have approximately the same envelope wave function and the calculated lifetimes will be almost correct. It is difficult to state the degree of impurity overlap that invalidates the theory.

We may, however, put a minimum limit on the spontaneous radiative recombination lifetime an electron or hole may have in a direct band gap semiconductor. This lifetime is that which occurs for interband transitions when a carrier can recombine with carriers of the opposite sign, occupying all states allowed by momentum conservation. Under these assumptions, each electron would have four holes, or each hole would have two electrons, to recombine with. Since the impurity states employ the phase space provided by the energy band states, it should be clear that recombination to impurity states cannot provide a lower lifetime than this minimum value.

Using Eq. (3) and (5) and summing over electromagnetic modes, the probability $\mathcal{R}_{vc}$ for a spontaneous radiative transition between a conduction band state and an empty valence band state of the same wave number is given by

$$\begin{aligned}\mathcal{R}_{vc}&=4\pi/n^2(e^2|P_{vc}|^2{}_{\text{av}}/\omega m^2)\rho(\hbar\omega)\\&=(4ne^2\omega/c^3m^2\hbar)|P_{vc}|^2{}_{\text{av}}.\end{aligned}\tag{19}$$

The minimum radiative lifetimes for electrons and holes, $(1/\tau_n)_{\text{min}}$ and $(1/\tau_p)_{\text{min}}$, will be given by

$$(\tau_n)_{\text{min}}=\tfrac{1}{2}(\tau_p)_{\text{min}}=1/4\mathcal{R}_{vc}=c^3m^2\hbar^2/16ne^2E_G|P_{vc}|^2.\tag{20}$$

For GaAs, $(\tau_n)_{\text{min}}=0.31$ nsec and $(\tau_p)_{\text{min}}=0.62$ nsec. For other direct band gap semiconductors the minimum lifetimes will scale roughly with the inverse of the band gap. In the case where a population inversion exists and the electromagnetic modes are highly excited, it is possible for the electron distribution to decay even faster than $(\tau_n)_{\text{min}}$ suggests.

The minimum radiative lifetimes represent a limit below which the lifetimes due to recombination involving impurity states is clearly invalid. The region of validity would be those doping concentrations at which carrier freeze out is observed to occur at low temperatures. With Zn acceptors in GaAs, freeze out is no longer observed in crystals with carrier concentrations above a few times 10^{18} cm^{-3}. For $p_A=2\times10^{18}$ cm^{-3} in GaAs, the electron lifetime at low temperatures is approximately 1 nsec, or approximately 3 times the minimum radiative electron lifetime.

We would estimate, therefore, that a proper test of the validity of band to impurity recombination would be that the low-temperature lifetime calculated for some impurity concentration would be at least a few (2 or 3) times larger than the minimum radiative lifetimes resulting from band to band transitions. For higher impurity concentrations overlap between adjacent impurities will cause the carrier wave functions to be more band like than localized.

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