

# Edge luminescence of direct-gap semiconductors

A. P. Levanyuk and V. V. Osipov

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An analysis is made of the theory of the luminescence spectra of semiconductors with direct optical transitions involving recombination of nonequilibrium carriers whose energies are close to the band gap edges. The usual formulation of the theory of recombination is employed, i.e., given densities of free electrons and holes are assumed. The first part of the review is concerned with the luminescence (of the exciton, interband, impurity, or interimpurity type) of lightly doped semiconductors. Unsolved problems are noted and it is stressed particularly that the interband luminescence spectrum is governed largely by the interaction of carriers and by the mechanisms of their scattering, but in practice this has been ignored so far in the development of the theory and in the interpretation of the experimental results. The second (main) part of the review is devoted to the luminescence of heavily doped semiconductors. It is shown that the nature of the electron spectrum of such semiconductors, involving formation of density-of-states "tails" and broadening of the impurity levels, is manifested clearly in this case. It is stressed that the distribution of nonequilibrium carriers between localized states corresponding to a continuous spectrum is usually quite different from the quasiequilibrium distribution, i.e., it cannot be described by introduction of the quasi-Fermi level. An allowance for this circumstance makes it possible to explain a great variety of seemingly contradictory experimental data on the luminescence spectra of heavily doped semiconductors. The deviation of the carrier distribution from the quasiequilibrium case is manifested also in transient characteristics of the luminescence, and it also governs the characteristic features of radiative recombination in strongly compensated heavily doped semiconductors, which can be regarded as one of the models of amorphous semiconductors. It is pointed out in conclusion that the proposed concepts can account for the special features of the characteristics of electroluminescent structures made of heavily doped semiconductors.

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## INTRODUCTION

Edge luminescence is the spontaneous radiation of energy close to the band gap of a semiconductor, which appears as a result of recombination of nonequilibrium carriers. Back in 1923, Losev<sup>1</sup> detected and interpreted correctly the recombination radiation which appeared as a result of carrier injection in silicon carbide. In 1952, luminescence was observed in the case of germanium *p*–*n* junctions,<sup>2,3</sup> whereas in 1955 the same observation was made<sup>4</sup> in the case of junctions fabricated from GaAs, a material with direct optical transitions exhibiting most clearly the effects associated with radiative recombination in semiconductors.

An enormous amount of work has been done since on

the luminescence of semiconductors. This is primarily due to the fact that luminescence investigations provide one of the most sensitive and most widely used experimental methods for investigating specific features of the energy spectrum and transport properties of crystals. The interest in luminescence has increased further after the discovery<sup>5</sup> of stimulated emission from GaAs and fabrication of injection lasers,<sup>6–8</sup> particularly heterolasers,<sup>9</sup> and also spontaneous radiation sources characterized by a high efficiency and fast response.<sup>10–18</sup> In the course of these investigations a great variety of dependences has been observed and the results of different authors have frequently been in direct contradiction with one another, as well as with the theoretical concepts used in the interpretation.<sup>7,18–21</sup>

Usually<sup>19-21</sup> the luminescence spectrum  $\Phi(\omega)$  is deduced from the Kirchoff law using the frequency dependence of the absorption coefficient  $\alpha(\omega)$ :  $\Phi(\omega) \propto \omega^2 \alpha(\omega) \exp(-\omega/T)$  (this law is also used in the calculation of the radiative recombination rates<sup>22</sup>). In many cases this approach is permissible but, as stressed below, the spectrum  $\Phi(\omega)$  is governed by those details of the dependence  $\alpha(\omega)$  which are usually ignored when absorption is considered. For example, in the calculation of the luminescence spectra representing recombination of free electrons and holes it is necessary to know the dependence  $\alpha(\omega)$  at photon energies  $\omega$  close to the band gap  $E_g$ . In the case of direct-gap semiconductors it is usual<sup>19-21</sup> to assume that  $\alpha(\omega) \propto \sqrt{\omega - E_g}$ , which is quite unjustified because this dependence is valid only in the case of sufficiently large values of  $\omega - E_g$  when the Coulomb interaction between electrons and holes, and their scattering can be ignored.<sup>18,23</sup> Allowance for the pure Coulomb (without screening) interaction between electrons and holes gives rise to a step in the dependence  $\Phi(\omega)$  (see Sec. 1 c). The true form of  $\Phi(\omega)$ , particularly at long wavelengths, is governed by the screening of the Coulomb interaction and the scattering of carriers. Thus, it would be more natural to formulate the problem of direct calculation of the luminescence spectra rather than to make allowance for details of the dependence  $\alpha(\omega)$  important for luminescence. This will be the approach adopted in the present review. It allows automatically for a possible nonequilibrium nature of the distribution of carriers between the states, which is also very important.

In fact, it would seem that the luminescence spectrum can be reconstructed from the experimentally determined dependence  $\alpha(\omega)$ , as shown in Ref. 20. However, the luminescence spectrum obtained in this way may differ considerably from that observed experimentally. This is due to the fact that, in contrast to absorption, luminescence is an essentially nonequilibrium process. Luminescence is usually observed under strong excitation conditions when the distribution of nonequilibrium carriers between the states may differ considerably from the equilibrium distribution, i. e., in only a few cases can the distribution be described by the introduction of quasi-Fermi levels for electrons and holes.

The nonequilibrium nature of luminescence is manifested particularly clearly in the case of heavily doped semiconductors, and most of the experimental material has been obtained on such semiconductors. Interest in these semiconductors is primarily due to the high efficiency of radiative recombination in these materials<sup>12-17</sup> and also because they represent convenient objects for investigating the properties of disordered systems.<sup>24</sup> The difficulties which are encountered in the interpretation of the experimental data on the luminescence of heavily doped semiconductors are associated also with the characteristic features of their electron spectra.<sup>25-28</sup> In the reviews and monographs published so far these features are discussed, if at all, only cursorily and frequently in an inconsistent manner. Recent theoretical<sup>29-37</sup> and experimental investigations,

to which references will be made later, have made clear the complex nature of the luminescence emitted by heavily doped semiconductors. The situation is far from trivial, contrary to the earlier suggestions.<sup>7,18,21,38</sup> These nontrivial features of the luminescence of these materials and their importance in the interpretation of the experimental data form a major part of the present review. We shall be concerned mainly with semiconductors exhibiting direct allowed optical transitions, since these materials (GaAs, InSb, InAs) have been investigated most thoroughly in the experimental sense, and the individual properties of shallow impurities are not very important in these semiconductors.

Depending on the method of carrier generation, we can distinguish the following kinds of luminescence: photoluminescence resulting from illumination of a crystal with short-wavelength light; cathodoluminescence excited by a beam of fast electrons; breakdown electroluminescence associated with avalanche generation of carriers in strong electric fields; injection electroluminescence resulting from the injection of carriers from the contacts, mainly from  $p-n$  junctions. An analysis of the luminescence spectra will be made below employing the usual formulation of the theory of recombination, i. e., assuming given densities of free carriers. The relationship between the densities of free electrons and holes and the rate of pumping under various excitation conditions is a problem on its own because the carrier densities are usually governed not by radiative recombination but by some form of non-radiative recombination.

The distributions of free electrons and holes can usually be described by introducing quasi-Fermi levels  $F_n$  and  $F_p$ , respectively. Therefore, for given carrier densities the problem reduces to finding the distribution of carriers between localized states. Special attention will be given to this distribution. However, we must bear in mind that the method of excitation of nonequilibrium carriers may, in principle, influence the distribution. In particular, this is true in the case of the photoluminescence excited by a source of light with a fairly wide spectral band. Moreover, it is found that in some cases  $\Phi(\omega)$  is not governed uniquely by the density of the electron states and the distribution function. Thus, in general, even the knowledge of the carrier distribution and of  $\alpha(\omega)$  is insufficient to find the luminescence spectrum of a compensated heavily doped semiconductor (see Sec. 2 e).

An analysis of the fairly complex phenomenon of the luminescence of heavily doped semiconductors, which is discussed in the second part of the present review, will be introduced by a description of the main radiative recombination mechanisms active in lightly doped semiconductors. It will be stressed that even in the case of lightly doped semiconductors there are still many unsolved but very important (in the interpretation of the experimental data) problems. A discussion of the status of the theory in this case is absolutely essential also for the understanding of the further discussion and comparisons.

# 1. LUMINESCENCE OF LIGHTLY DOPED SEMICONDUCTORS

## a) Probabilities of spontaneous radiative transitions

The wave functions of an electron and a hole with energies close to the band gap edges can be written as follows if the effective mass approximation is used<sup>39</sup>

$$\Psi_i = F_i(\mathbf{r}) U_c(\mathbf{r}) \exp(i\mathbf{k}_{c0}\mathbf{r}), \quad \Psi_f = F_f(\mathbf{r}) U_v(\mathbf{r}) \exp(i\mathbf{k}_{v0}\mathbf{r}), \quad (1.1a)$$

where  $U_c(\mathbf{r}) \exp(i\mathbf{k}_{c0}\mathbf{r})$  and  $U_v(\mathbf{r}) \exp(i\mathbf{k}_{v0}\mathbf{r})$  are the Bloch functions representing the bottom of the conduction band and the top of the valence band, which correspond to the same point in quasimomentum space in the case of direct-gap semiconductors and, as a rule, we have  $\mathbf{k}_{c0} = \mathbf{k}_{v0} = 0$  (Fig. 1);  $F_i$  and  $F_f$  are the modulating functions representing solutions of the wave equation in the effective mass method<sup>39</sup> and normalized to a standard volume of the lattice  $V$ . In the case of free carriers, we have

$$F_i(\mathbf{r}) = V^{-1/2} \exp(i\mathbf{k}_i\mathbf{r}), \quad F_f(\mathbf{r}) = V^{-1/2} \exp(i\mathbf{k}_f\mathbf{r}), \quad (1.1b)$$

and in the case of carriers localized at a shallow impurity level,

$$F_i = (\pi a_{e,h}^3)^{-1/2} \exp(-r/a_{e,h}), \quad (1.1c)$$

where  $a_{e,h}^{-1} = a_{e,h}$  is the Bohr radius of an electron or a hole, respectively. Bearing in mind that the function  $F(\mathbf{r})$  varies slowly over distances of the order of the lattice constant, we find that the probability of a radiative transition from a state  $i$  to a state  $f$  in a semiconductor with direct allowed optical transitions can be represented in the form<sup>23</sup>

$$w_{i,f} = A \left| \int F_f^*(\mathbf{r}) F_i(\mathbf{r}) d\mathbf{r} \right|^2, \quad (1.2)$$

where

$$A = \frac{4e^2 \pi \omega \hbar}{m_0^2 c^2 v_0^3} \left| \int U_c^*(\mathbf{r}) \nabla_{\perp} U_v(\mathbf{r}) d\mathbf{r} \right|^2 = \frac{2\bar{n}}{3 \cdot 137} \frac{E_g}{m_0 c^2} \frac{\omega}{\hbar} \frac{E_g + \Delta}{E_g + (2/3)\Delta}, \quad (1.2a)$$

$\omega$  is the photon energy;  $\bar{n}$  is the refractive index;  $v_0$  is the volume of a unit cell;  $m_0/\bar{m}_e = m_0/m_e - 1$ ;  $m_0$  is the mass of an electron in vacuum. The last equality in Eq. (1.2a) applies to the Kane model of the energy spectrum<sup>23</sup> ( $\Delta$  is the spin-orbit splitting).

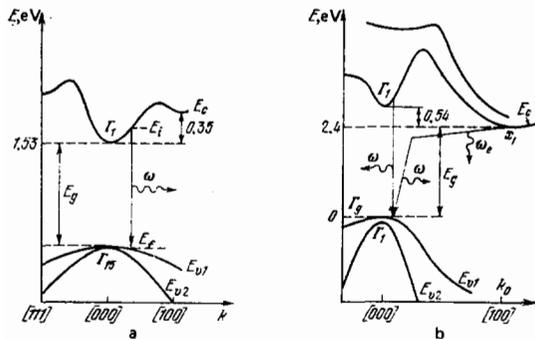


FIG. 1. Dependence of the electron energy on the quasimomentum in semiconductors with direct (a, with GaAs as an example) and indirect (b, with GaP as an example) optical transitions. The arrows identify the direct and indirect transitions accompanied by the emission of a photon and an optical phonon of energy  $\omega_1$ .

Substituting Eq. (1.1b) in Eq. (1.2), we find that the probability of an interband transition, i.e., the probability of radiative recombination of free electrons and holes, is given by<sup>23</sup>

$$w_{c,v} = A \delta_{\mathbf{k}_i, \mathbf{k}_f}. \quad (1.3)$$

The probability of a band-impurity transition, i.e., for example, the probability of recombination of a free electron with a hole localized at an acceptor, can be deduced from Eqs. (1.1b), (1.1c), and (1.2) (Ref. 40):

$$w_{c,a} = \frac{A64\pi\alpha^3}{V(\alpha^2 - k^2)^4} = \frac{A64\pi\alpha^3}{V(\alpha^2 - k^2)^4} \left( \frac{\alpha^2}{\alpha^2 - k^2} \right)^i = \frac{W_0}{V} \left( \frac{\alpha^2}{\alpha^2 - k^2} \right)^i. \quad (1.4)$$

The probability of an interimpurity (donor-acceptor) transition, i.e., the probability of recombination of an electron bound to a donor with a hole localized at an acceptor, is governed by the overlap integral (1.2) of two hydrogen-like functions (1.1c) and in the case when  $a_e \gg a_h$ , this probability is<sup>41</sup>

$$w_{d,a} = 64A \left( \frac{a_h}{a_e} \right)^3 \exp\left(-\frac{2r}{a_e}\right) \equiv v_0 \exp\left(-\frac{2r}{a_e}\right), \quad (1.5)$$

where  $r$  is the distance between the donor and acceptor.

Equation (1.2) is derived ignoring the interaction between an electron and a hole (as well as other many-body effects). We shall generalize Eq. (1.2) by representing the integral in this equation in the form

$$\int F_f^*(\mathbf{r}) F_i(\mathbf{r}) d\mathbf{r} = \int F_h(\mathbf{r}_h) F_e(\mathbf{r}_e) \delta(\mathbf{r}_e - \mathbf{r}_h) d\mathbf{r}_e d\mathbf{r}_h = \int F(\mathbf{r}_h, \mathbf{r}_e) \delta(\mathbf{r}_e - \mathbf{r}_h) d\mathbf{r}_e d\mathbf{r}_h,$$

where  $F(\mathbf{r}_h, \mathbf{r}_e)$  is the wave function of an electron and a hole. If allowance is made for the interaction between electrons and holes, it is found that  $F(\mathbf{r}_h, \mathbf{r}_e) \neq F(\mathbf{r}_h)F(\mathbf{r}_e)$ . However, in the case of a homogeneous medium we have  $F(\mathbf{r}_h, \mathbf{r}_e) = \Psi(\mathbf{R})\varphi(\mathbf{r})$ , where  $\mathbf{R}$  is the coordinate of the center of mass of an electron and a hole and  $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h$ . Thus, it follows from Eq. (1.2) that

$$w_{e,h} = \left| A \int \varphi_i(\mathbf{r}) \delta(\mathbf{r}) d\mathbf{r} \int \Psi(\mathbf{R}) d\mathbf{R} \right|^2. \quad (1.6)$$

In the case of a freely moving electron-hole pair we have  $\Psi(\mathbf{R}) = \Psi_0(\mathbf{R}) = V^{-1/2} \exp(i\mathbf{k}\mathbf{R})$ , where  $\mathbf{k} = \mathbf{k}_e + \mathbf{k}_h$ ,  $\alpha\varphi_i(\mathbf{r})$  is a hydrogen-like wave function representing the relative motion of an electron and a hole in a state  $i$ . We then have<sup>23,42</sup>

$$w_{e,h}(\mathbf{k}, i) = AV |\varphi_i(0)|^2 \delta_{\mathbf{k}, 0}. \quad (1.7)$$

The scattering effects can also be included in the formulas (1.2) and (1.6) if the wave functions  $F(\mathbf{r})$  and  $\Psi(\mathbf{R})$  are not regarded as plane waves but as suitably modified functions (see below). A rigorous analysis of these points can be carried out conveniently using the Green's function formalism.<sup>26,43,44</sup>

## b) Exciton luminescence

In the case of a semiconductor with a small effective mass of one of the carriers, an electron and a hole form a Wannier-Mott exciton in a bound state.<sup>42-44</sup>

Luminescence resulting from its annihilation is known as exciton luminescence. Using Eq. (1.7) for the intensity of the principal spectral line of this luminescence, we find that (in particular, when  $i = 0$ )

$$I_{ex}(\omega) = \frac{2\omega}{V} \sum_{\mathbf{k}} w_{e,h}(\mathbf{k}, 0) |f_{ex}(\mathbf{k})|^2 \delta(\omega - E_{ex}) = 2\omega A \frac{f_{ex}^2(0)}{\pi a_0^3} \delta(\omega - E_{ex}), \quad (1.8)$$

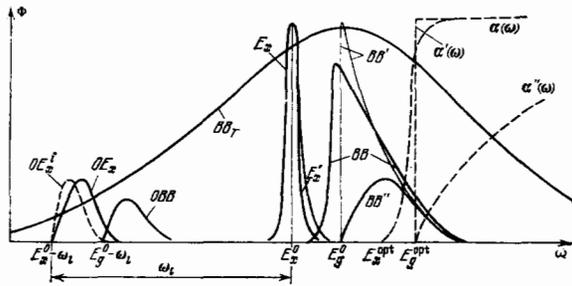


FIG. 2. Qualitative form of the luminescence spectra resulting from exciton and interband recombination. Here,  $BB$  and  $\alpha(\omega)$  are the luminescence and absorption spectra due to interband transitions;  $BB'$  and  $\alpha'(\omega)$  are the luminescence and absorption spectra due to the same transitions but without allowance for the interaction and scattering of carriers;  $BB'$  and  $\alpha'(\omega)$  are the same spectra with allowance only for the Coulomb interaction between electrons and holes;  $OBB$  is the optical replica line of interband luminescence;  $E_x$  is the spectrum due to annihilation of excitons;  $E_x'$  is the same spectrum but when only the direct transitions are allowed for;  $OE_x$  is the optical replica line of the exciton luminescence;  $OE_x'$  is the principal exciton luminescence line of indirect semiconductors;  $BB_T$  is the edge luminescence spectrum at high temperatures.

where  $E_{ex} = E_{ex}^0 + (\hbar^2 k^2 / 2m^*)$  is the exciton energy;  $a_B$  is the Bohr radius of an exciton;  $m^* = m_e m_h / (m_e + m_h)$  is the reduced mass of an electron and a hole;  $f_{ex}^i(k)$  is the distribution function of nonequilibrium excitons in a state  $i$ ; the factor 2 allows for the spin conservation in an optical transition.<sup>19,23</sup> If we assume that  $f_{ex}^0$  is the Maxwellian distribution, then  $f_{ex}^0(0) = n_{ex} / N_{ex}$ , where  $n_{ex}$  is the concentration of excitons and  $N_{ex} \propto T^{3/2}$  is the effective number of exciton states.<sup>39</sup> The radiative recombination rate, i.e., the number of electron-hole pairs recombining per unit volume and per unit time

$$R_{rad} = \int \frac{1}{\omega} \Phi(\omega) d\omega, \quad (1.9)$$

can be deduced from Eq. (1.8)

$$R_{ex} = \frac{n_{ex}}{\tau_{ex}}, \quad \text{where } \tau_{ex} = \pi N_{ex} a_B^3 A^{-1}. \quad (1.10)$$

The exciton lifetime  $\tau_{ex}$  is extremely short for the majority of direct-gap semiconductors. For example, in the case of GaAs, we have  $\tau_{ex} \sim 10^{-10}$  sec [this follows from the theoretical estimate based on Eq. (1.2a) and from the experimental data<sup>18,48</sup> that  $A^{-1} \approx 0.3 \times 10^{-9}$  sec]. However, the time required to fill a state with  $k=0$ , governed by inelastic collisions, can exceed  $\tau_{ex}$  at low temperatures and moderate exciton concentrations.<sup>1)</sup> Under these conditions we can expect a rapid loss of carriers from the  $k=0$  state and the use of the Maxwellian distribution in the calculation of  $f_{ex}(0)$  is no longer justified. To the best of our knowledge, a rigorous calculation of  $f_{ex}(k)$  has not yet been carried out, although the true form of this distribution at low values of  $k$  governs not only the exciton annihilation rate but also the shape of the exciton luminescence spectrum.

According to Eq. (1.8), the exciton luminescence spectrum can be regarded as a  $\delta$  function. The finite

<sup>1)</sup> At high exciton concentrations their interaction becomes important but this is a separate problem.<sup>45</sup>

width of an exciton line (Fig. 2) is governed by the scattering processes,<sup>43,44</sup> when the  $\delta$  function has to be replaced with a bell-shaped function of width  $\Gamma \approx \hbar / \tau_0$ , where  $\tau_0$  is the exciton lifetime in the state with  $k=0$ . This function is close to Lorentzian, i.e.,

$$\delta(\omega - E_{ex}^0) \rightarrow \frac{1}{\pi} \frac{\Gamma(\omega)}{(\omega - E_{ex}^0 + \Delta(\omega))^2 + \Gamma^2(\omega)}, \quad (1.11)$$

when excitons are scattered mainly by impurities or acoustic phonons and the electron-phonon interaction is weak.<sup>43,44</sup> We then have  $\Delta \approx \Gamma \approx \hbar / \tau_0$ , where  $\tau_0^{-1} = \tau_{i0}^{-1} + \tau_{i0}^{-1}$ , and the frequencies of the scattering by impurities and phonons are proportional to the corresponding concentrations ( $\tau_{i0}^{-1} \propto N$ ,  $\tau_{i0}^{-1} \propto T$ ). Thus in the case of pure semiconductors and moderately low temperatures, the width of the principal exciton luminescence line is proportional to  $T$ , as indicated by Eq. (1.11). However, the coefficient of proportionality is much less than unity for most semiconductors.<sup>43</sup>

Deviations from the Lorentzian profile of the luminescence line (Fig. 2) are associated, in particular, with the contribution of indirect transitions. These occur without quasimomentum conservation because of the scattering processes. In other words, when a scatterer participates, exciton annihilation with  $k \neq 0$  is possible. The probability of such transitions is low compared with direct transitions and, therefore, in spite of the fact that the majority of excitons is characterized by  $k \neq 0$ , their annihilation appears only in the short-wavelength wing of the luminescence line (Fig. 2). Spreading of the luminescence spectrum toward shorter wavelengths can be described as an increase of the coefficient  $\Gamma(\omega)$  in Eq. (1.11) on increase in frequency.

In the case of real semiconductors the exciton luminescence spectrum can have a fairly complex form.<sup>46,47</sup> Thus, at low temperatures the principal line is due to the annihilation of excitons bound to defects. The fine structure of the exciton line can be determined if we allow for the polariton effects, i.e., for the mutual influence of the electro-magnetic field and excitons.<sup>43,44</sup> Some experiments<sup>46</sup> have revealed luminescence associated with the annihilation of excitons in one of the lowest excited  $s$  states. The intensity of such luminescence obeys  $\Phi_n \approx a_B^{-3}(n) f_{ex}^a(0) \propto n^{-3} \exp[(E_{ex}^0 - E_s) / n^2 T]$ , i.e., it decreases faster than  $n^{-3}$ , where  $n$  is the principal quantum number in the Coulomb problem.<sup>2)</sup>

In addition to the principal line, an optical replica line representing the annihilation of an exciton and simultaneous emission of a longitudinal optical phonon is also important. It is shifted in the direction of longer wavelengths relative to the principal exciton line by an energy equal to the optical phonon energy  $\omega_1$  (Fig. 2). In the case of luminescence involving optical phonons the selection rule of quasimomentum (1.7) is not obeyed, i.e., the optical replica line is entirely due to

<sup>2)</sup> This does not apply to high values of  $n$  when  $A_B(n)$  becomes greater than the screening length or the scattering length. Screening and scattering cause the higher excited exciton levels to merge with the continuous spectrum, reducing effectively the band gap  $E_g^0$  (See Sec. 1. c).

indirect optical transitions. Consequently, excitons with any vector  $k$  contribute to this line. Its profile is governed by the density of the exciton states  $f_{ex}(k)$  and by the dependence on  $k$  of the constant of the interaction between an exciton and an optical phonon. This constant<sup>44</sup> is known to be proportional to  $k$  and the characteristics of  $f_{ex}(k)$  at low values of  $k$  are not significant so that in the case of nondegenerate excitons the profile of an optical replica line is described well<sup>46</sup> by the function  $(\omega - E_{ex}^0 + \omega_1)^{3/2} \exp(-\omega/T)$ . Since the optical replica line is due to the annihilation of excitons with any value of  $k$  and the interaction with longitudinal optical phonons is strong, the rate of recombination accompanied by the emission of such phonons can be considerable<sup>46</sup>:

$$R_{opt} = An_{ex} \frac{(m_e - m_h)^2}{2m^* (m_e + m_h)} \frac{T}{\omega_1} \left( \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_\infty} \right), \quad (1.12)$$

where  $\epsilon_0$  and  $\epsilon_\infty$  are the static and high-frequency (optical) permittivities.

When the bottom of the conduction band and the top of the valence band differ by  $k_0$  (Fig. 1b), direct recombination of an electron and a hole is generally impossible. In the case of such indirect-gap semiconductors the annihilation of an exciton is usually accompanied by the emission of an optical phonon and the corresponding line is the principal one in the exciton luminescence spectrum. Since the optical phonons which are then emitted are characterized by  $k \approx k_0$ , we can ignore the dependence of the exciton-optical phonon interaction constant on  $k$ . Consequently, the profile of the exciton luminescence line of indirect-gap semiconductors is described accurately<sup>46</sup> by the function  $(\omega - E_{ex}^0 - \omega_1)^{1/2} \times \exp(-\omega/T)$ , i.e., it differs greatly from the profile of the principal exciton line and its optical replica in the case of direct-gap semiconductors (Fig. 2).

### c) Interband radiative recombination

In the case of direct-gap semiconductors the spectral dependence of the luminescence, emitted per unit volume as a result of recombination of free electrons and holes, is described by the expression<sup>3)</sup>

$$\Phi_{c,v}(\omega) = \frac{2\omega}{T^2} \sum_{k_e, k_h} w_{c,h}(k_e, k_h) f_c(k_e) f_v(k_h) \delta(\omega - E_g^0 - \epsilon_e - \epsilon_h), \quad (1.13)$$

where  $E_g^0$  is the band gap of a semiconductor;  $\epsilon_e$  and  $\epsilon_h$  are the kinetic energies of an electron and a hole;  $f_c$  and  $f_v$  are the distribution functions of electrons and holes between the states in free and valence bands. Since the relaxation time of the free-carrier energy is usually less than the recombination time, it follows that  $f_c$  and  $f_v$  can be regarded as the Fermi functions with the electron and hole quasi-Fermi levels  $F_n$  and  $F_p$ , respectively.

When electrons and holes are not degenerate, it is essential to allow for the interaction between them. In other words, interband luminescence should be regarded as a consequence of the annihilation of excitons which

are in states of a continuous spectrum. Such exciton states can be described conveniently by the wave function depending on  $k = k_e + k_h$ ,  $K = k_e - k_h$ , where  $k_e$  and  $k_h$  are the wave vectors of an electron and a hole which are an infinite distance apart. Going over in Eq. (1.13) to the variables  $K$  and  $k$ , and applying Eq. (1.7), we find that in the case of nondegenerate carriers

$$\Phi_{c,v}(\omega) = \frac{A\omega}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} (\omega - E_g^0)^{1/2} \Delta \exp \Delta \operatorname{sh}^{-1} \Delta \exp \left( \frac{F_n - F_p - \omega}{T} \right), \quad (1.14)$$

where  $\Delta = \pi \sqrt{E_{ex}} / (\omega - E_g^0)$ . According to Eq. (1.14), the function  $\Phi_{c,v}(\omega)$  increases abruptly at  $\omega = E_g^0$  from zero to a finite value and decreases exponentially at short wavelengths ( $BB'$  in Fig. 2), i.e.,  $\Phi_{c,v}(\omega) \propto \Theta(\omega - E_g^0) \exp(-\omega/T)$ ; on the other hand, it follows from Eqs. (1.13) and (1.3) that  $\Phi_{c,v}(\omega) \propto (\omega - E_g^0)^{1/2} \exp(-\omega/T)$ .<sup>4)</sup> Such a luminescence line is represented by curve  $BB''$  in Fig. 2, which shows how strongly the interaction between carriers influences the shape of the spectrum. For example, the half-width of the line corresponding to the curve  $BB''$  is  $1.8T$ , whereas in the case of the  $BB'$  curve it is  $0.7T$ . The half-width of the luminescence spectrum of the purest semiconductors usually has an intermediate value<sup>20,45,46,49</sup> and the line profile ( $BB$  in Fig. 2) is smoother than that predicted by Eq. (1.14). This discrepancy is due to the fact that Eq. (1.14) is derived ignoring the scattering of carriers and other many-body effects. For example, the recombination of an electron with a hole accompanied by the simultaneous emission of one, two, etc. longitudinal optical phonons leads, as in the exciton luminescence case, to corresponding optical replica lines ( $OBB$  in Fig. 2).

It follows that determination of the shape of the interband luminescence spectrum of direct-gap nondegenerate semiconductors is a very difficult task because one has to allow for the Coulomb interaction between carriers and for their scattering, and for the fact that indirect transitions contribute to the luminescence. This task has not yet been tackled fully. Qualitatively, many-body effects can result in the following changes in the luminescence spectrum.

The finite lifetime in each state, i.e., the energy indeterminacy, shifts somewhat the spectral maximum of the luminescence toward longer wavelengths (Fig. 2) so that a long-wavelength wing of the interband luminescence line appears in the spectrum. These effects can be reproduced by replacing the  $\delta$  function in Eq. (1.13) with some function of finite width, by analogy with Eq. (1.11). As in the exciton luminescence case (Sec. 1b) the observed spreading compared with Eq. (1.14) toward shorter wavelengths<sup>45,49</sup> is associated with the contribution of indirect transitions which lift the restrictions imposed by the selection rule (1.7) in respect of the quasimomentum  $k$ . The long-wavelength wing includes also a contribution of the luminescence corresponding to the annihilation of excitons from excited states in the discrete spectrum. When tempera-

<sup>3)</sup> In the case of semiconductors with a complex valence band (Fig. 1a) the expressions for  $\Phi_{c,v}(\omega)$  represent a sum of the bands of light, heavy, and spin-split-off holes.<sup>19</sup>

<sup>4)</sup> This formula is given in many monographs and is used without any justification in the analysis of experimental results.

ture is increased, the scattering by phonons becomes stronger so that the interband luminescence spectrum spreads even further toward longer wavelengths, and the optical replica lines increase in intensity in accordance with Eq. (1.12) and become broader. At sufficiently high temperatures the lines corresponding to different edge luminescence channels merge so that the fall of the luminescence intensity on the long-wavelength side becomes monotonic (Fig. 2). Experimental investigations of the luminescence and absorption have shown that the long-wavelength fall is described by  $\exp(-\omega/T)$  over a wide range of  $\omega$  and  $T$ , in accordance with the Urbach rule. A convincing theoretical justification of this rule is not yet available, although an analysis of this question has a long history behind it.<sup>7,18,21,23,43</sup>

Naturally, many-body effects influence also the frequency dependence of the absorption coefficient  $\alpha(\omega)$ . If we use the Einstein relationships between the probability of spontaneous emission of a photon and the probability of its absorption,<sup>7,8,19</sup> we can represent  $\alpha(\omega)$  in the form

$$\alpha(\omega) = \frac{2\pi^2 c^2 \hbar^3}{V \omega^2 \hbar^2} \sum_{\mathbf{k}_e, \mathbf{k}_h} w_{e, h}(\mathbf{k}_e, \mathbf{k}_h) [1 - f_c(\mathbf{k}_e)] \times [1 - f_v(\mathbf{k}_h)] \delta(\omega - E_g^{opt} - \epsilon_e - \epsilon_h). \quad (1.15)$$

It follows from Eqs. (1.13) and (1.15) that in the case of nondegenerate carriers and when  $E_g^{opt} = E_g^0$ , we have

$$D_{c, v}(\omega) = \frac{\bar{n}^2 \omega^3 \alpha(\omega)}{\pi^2 \hbar^3 c^2} \exp\left(\frac{F_n - F_p - \omega}{T}\right) = \frac{\bar{n}^2 \omega^3 \alpha(\omega)}{\pi^2 \hbar^3 c^2} \frac{np}{n_i^2} \exp\left(-\frac{\omega}{T}\right). \quad (1.16)$$

This relationship can be obtained also from thermodynamic considerations,<sup>22</sup> which—strictly speaking—are applicable only to equilibrium luminescence. The assumption of thermodynamic equilibrium is not used in the derivation of Eq. (1.16), but no allowance is made for the polaron effects resulting in a long-wavelength (Stokes) shift of the luminescence lines compared with the corresponding absorption lines. Due to these effects the values of  $E_g^0$  and  $E_g^{opt}$ , and also  $m_e$  and  $m_h$  in Eqs. (1.13) and (1.15) can differ considerably. In the case of solids, as for molecules, the Stokes shift can be explained by the Franck-Condon principle.<sup>50</sup> In the case of semiconductors this means that the creation of an electron-hole pair on absorption of a photon occurs with the nuclei remaining in a frozen configuration. Then, as a result of the interaction of a carrier with lattice ions, the configuration becomes locally distorted and this produces a polaron<sup>39</sup> characterized by a large effective mass and a low energy compared with a free carrier. Radiative transitions between the polaron states then determine the luminescence. In the case of majority semiconductors a weak-coupling polaron is then formed<sup>39</sup> and the reduction in the energy due to the formation of electron and hole polarons, i.e., the difference between the optical  $E_g^{opt}$  and thermal  $E_g^0$  band gaps appearing in Eqs. (1.15) and (1.13), respectively, represents approximately

$$E_g^{opt} - E_g^0 \approx \Delta_{pol}^h + \Delta_{pol}^e = \frac{\epsilon(0) - \epsilon(\infty)}{\epsilon(\infty)} \sqrt{3.2 \omega_1} (\sqrt{I_a} + \sqrt{I_d}), \quad (1.17)$$

where  $I_a$  and  $I_d$  are the ionization energies of hydrogen-like acceptors and donors. According to estimates, in the case of some direct-gap semiconductors, particularly GaAs, the value of  $\Delta_{pol}$  exceeds  $I_d$  and the exciton

binding energy. Therefore, without allowance for the polaron effect an interband luminescence line can be regarded as representing, in accordance with its energy position (Fig. 2), an exciton or impurity luminescence line, which is a typical error in the interpretation of the luminescence spectra of pure single crystals.

The electric field associated with a carrier causes not only displacements of ions, but also changes the electron and hole densities. If this effect is allowed for, an additional term appears on the right-hand side of Eq. (1.17). In fact, when the photon frequency is  $\omega \approx E_g^0 \gg \omega_M$ , where  $\omega_M$  is the Maxwellian relaxation frequency, the absorption of a photon occurs in the presence of a frozen electron and hole configuration, which then becomes modified and screens the field of the resultant carriers. This effect reduces the electron and hole energy by the correlation energy of an ionized gas per electron-hole pair<sup>51</sup> and this energy is equal to  $e^2/\epsilon r_0$ , where  $r_0$  is the Debye screening radius.

If carriers (for example, electrons) are degenerate, then  $r_0 < a_c$  and the Coulomb interaction between an electron and a hole becomes insignificant. This leads, in particular, to the disappearance of the exciton luminescence.<sup>45</sup> Calculations of  $\Phi(\omega)$  and  $\alpha(\omega)$  in accordance with Eqs. (1.13), (1.15), and (1.3) give the following results in the case of scalar effective masses<sup>52</sup>

$$D_{c, v}(\omega) = \frac{A \omega}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} \omega_1^{1/2} \left[ \exp\left(\frac{F_n - F_p}{T} - \frac{m^* \omega_1}{m_e T}\right) + 1 \right]^{-1} \times \left[ \exp\left(\frac{F_p - E_v}{T} - \frac{m^* \omega_1}{m_h T}\right) - 1 \right]^{-1}, \quad (1.18a)$$

$$\alpha(\omega) = A \frac{(2m^*)^{3/2} \epsilon^2}{2\omega^2 \hbar^2} \omega_1^{1/2} \left[ 1 - \exp\left(\frac{F_n - E_c}{T} - \frac{m^* \omega_1}{m_e T}\right) \right]^{-1} \times \left[ 1 + \exp\left(\frac{E_v - F_p}{T} - \frac{m^* \omega_1}{m_h T}\right) \right]^{-1}, \quad (1.18b)$$

where  $\omega_1 = \omega - E_g$ . It then follows from Eq. (1.18a) that the radiative recombination rate (1.9) in the case of interband transitions is

$$R_{c, v} = A \left(\frac{m_h}{m_h + m_e}\right)^{3/2} \frac{pn}{N_v} \quad \text{or} \quad R_{c, v} = Ap \equiv p_i \tau_{mlu}, \quad (1.19)$$

in the case of nondegenerate and strongly degenerate ( $F_n - E_c > T m_h/m_e$ ) electrons, respectively. Since in the case of nondegenerate semiconductors the Coulomb interaction between an electron and a hole is important, the interband radiative recombination coefficient  $W_{c, v} = N_v R_{c, v}/np$  depends strongly on the carrier density and temperature.<sup>48</sup> A greater difference between  $R_{c, v}$  and the value given by (1.19) can be expected in the case of heavily doped semiconductors (Sec. 2a).

Figure 3 demonstrates the great difference between the observed luminescence spectra of heavily doped semiconductors and those calculated using Eq. (1.18a); this difference increases on increase in the degree of doping of a semiconductor (compare curves 3 and 4 in Fig. 3). Moreover, the frequency dependence of the absorption coefficient  $\alpha(\omega)$  of a heavily doped semiconductor differs greatly from that calculated using Eq. (1.18b).<sup>21,27,28</sup> This difference is partly due to the fact that no allowance for the carrier scattering, which weakens the energy and quasimomentum selection rules, is made in Ref. 52. However, the main reason for the discrepancy between the theory and experiment is due

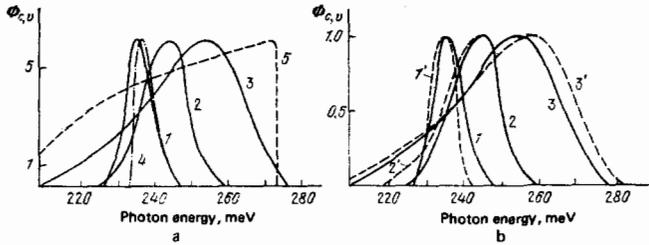


FIG. 3. Photoluminescence spectra of differently doped samples of *n*-type InSb at 4.2°K (Ref. 52): 1)  $n = 1.4 \times 10^{16} \text{ cm}^{-3}$ ; 2)  $n = 5 \times 10^{16} \text{ cm}^{-3}$ ; 3)  $2.5 \times 10^{17} \text{ cm}^{-3}$ ; 1')-3'), 4), 5) theoretical interband recombination spectra; 4) calculated using Eq. (1.18a) for  $n \geq 10^{16} \text{ cm}^{-3}$ ; 1')-3') calculated from Eq. (2.10) (Sec. 2b) for  $\eta = N_a (p + \theta n)^{-1} = 10^3$ ; 1')  $\gamma = 4.4 \text{ meV}$ ,  $\mu_n = E_n - E_c = 12 \text{ meV}$  ( $N_d \approx 1.3 \times 10^{16} \text{ cm}^{-3}$ ); 2')  $\gamma = 7.4 \text{ meV}$ ,  $\mu_n = 27 \text{ meV}$  ( $N_d \approx 5 \times 10^{16} \text{ cm}^{-3}$ ); 3')  $\gamma = 14.5 \text{ meV}$ ,  $\mu_n = 68 \text{ meV}$  ( $N_d \approx 2.5 \times 10^{17} \text{ cm}^{-3}$ ); 5) impurity recombination spectrum corresponding to Eq. (1.22),  $2.5 \times 10^{17} \text{ cm}^{-3}$ , and  $I_a = 30 \text{ meV}$ .

to the fact that a major change in the electron spectrum of a semiconductor resulting from fluctuations of the carrier density and of the charged impurity concentration<sup>25-28</sup> is ignored in the calculations of Ref. 52. Thus, the use of formulas (1.18) in the case of heavily doped semiconductors is doubtful even if only a rough estimate is required (Sec. 2a).

This does not apply to semiconductors with very low values of  $m_c$  and high  $\epsilon$ , which are degenerate even at such low electron densities that the influence of doping on the spectrum can be ignored. In particular, this applies to PbSnTe.

#### d) Impurity radiative recombination

The spectral intensity of the luminescence per unit volume, resulting from the recombination of free electrons with holes localized in acceptors in a direct-gap semiconductor, can be deduced from Eq. (1.4):

$$\Phi_{c,a}(\omega) = N_0 W_0 \omega \int_0^\infty \frac{I_1^2 \rho_c(\epsilon) \delta(\omega - \epsilon - E_g + I_a)}{(I_1 + \epsilon)^4 \{1 + \exp[(\epsilon - F_n + E_v)/T]\}} d\epsilon, \quad (1.20)$$

where  $I_a$  is the ionization energy of an acceptor;  $N_0$  is the concentration of neutral acceptors;  $I_1 = I_a m_h / m_e$ ;  $\epsilon$  is the kinetic energy of an electron;  $\rho_c(\epsilon)$  is the density of states given by<sup>39</sup>

$$\rho_c(\epsilon) = \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar} \right)^{3/2} \sqrt{\epsilon}. \quad (1.21)$$

It follows from Eqs. (1.20) and (1.21) that<sup>52</sup>

$$\Phi_{c,a}(\omega) = N_0 B \frac{\omega \sqrt{\omega - E_g + I_a}}{[1 + \exp(\omega + E_v + I_a - F_n)/T]} \frac{I_1^2}{(\omega - E_g + I_a + I_1)^4}, \quad (1.22)$$

where  $B = (W_0/2\pi^2)(2m_e/\hbar^2)^{3/2}$ . The last factor in Eq. (1.22) represents the dependence of the transition probability (1.4) on the electron wave vector. If  $(F_n - E_c) < I_1$ , it can be regarded as equal to unity because subject to this condition we find from Eq. (1.4) that

$$W_{c,a} = W_0 \equiv 64\pi A \sigma_0^2 = 64\pi A \left( \frac{\hbar^2}{2m_h I_a} \right)^{3/2}. \quad (1.23)$$

In this case the spectral line profile is independent of the individual characteristics of shallow acceptors and Eq. (1.22) applies also to semiconductors with an anisotropic effective mass of holes. The physical meaning of this result is that the characteristic value of the wave

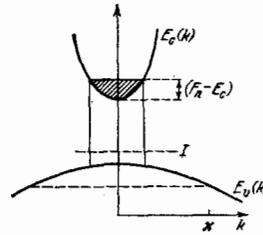


FIG. 4. Explanation of the absence of selection rules relating to quasimomentum in the case of impurity radiative recombination.

vector of the hole localized at an acceptor  $\kappa = a_n^{-1}$  is greater than the characteristic wave vector of an electron governed by the value of  $T$  or  $F_n - E_c$  (Fig. 4). It means that all the electrons are equally likely to recombine with localized holes and the spectral line profile is governed only by the electron state occupancy (Fig. 5). In the case of a nondegenerate semiconductor it follows from Eq. (1.22) that the energy of a spectral maximum is

$$\omega_m = E_g - I_a + 0.5T, \quad (1.24)$$

and the line half-width is then  $1.8T$ . In the degenerate case, we have

$$\omega_m = F_n - E_v - I_a - T \ln \left[ \frac{2(F_n - E_c)}{T} - 1 \right], \quad (1.25)$$

whereas the line width is governed by the value of  $F_n - E_c$ ; the characteristic energy of the fall of  $\Phi(\omega)$  at high frequencies is  $T$  (Fig. 5).

The rate of impurity radiative recombination deduced from Eqs. (1.9) and (1.22) is

$$R_{c,a} = W_0 N_0 n = 64\pi A (N_0 a_n^3) n, \quad (1.26)$$

which applies to nondegenerate and degenerate (if  $F_n - E_c < I_1$ ) electrons. The concentration of neutral acceptors (density of localized holes)  $N_0$  is found from<sup>5)</sup>

$$\frac{dN_0}{dt} = pN_0 W_p - nN_0 W_n - \nu_T N_0, \quad (1.27)$$

where  $W_n$  and  $W_p$  represent the coefficients of the capture of an electron and a hole by a neutral and a negatively charged acceptor, respectively. The coefficient  $\nu_T$  representing the rate of thermal release of holes from acceptor states to the band, can be expressed using the principle of detailed balance in terms of parameters of an equilibrium semiconductor<sup>54, 55</sup>:

$\nu_T = N_0^0 W_p p_0 / N_0^0 = W_p N_v \exp(-I_a/T)$ , where an allowance is made for the fact that  $N_0^0 / N_v^0 = \exp[(F_0 - E_v - I_a)/T]$ ; and  $p_0 = N_v \exp[(E_v - F_0)/T]$ ,  $F_0$  is the Fermi level under equilibrium conditions. The thermal release of electrons to the free band is ignored in Eq. (1.27) because

<sup>5)</sup> Strictly speaking, Eq. (1.27) applies to the case of injection luminescence when nonequilibrium carriers appear in a semiconductor by injection from a contact. In the case of photoexcitation, the right-hand side of Eq. (1.27) should be supplemented by the term  $\sigma_{ph} I_{ph} N$  ( $\sigma_{ph}$  is the photoionization cross section and  $I_{ph}$  is the density of the incident light flux) and  $p$  in Eq. (1.28) should be replaced with  $p + \sigma_{ph} J_{ph} W_p^{-1}$ . However, these corrections are usually unimportant because nonequilibrium holes are formed mainly by interband rather than impurity absorption.

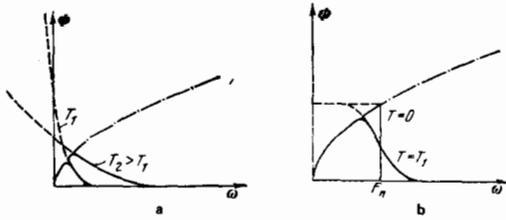


FIG. 5. Shape of the luminescence spectra in the case of impurity recombination: a) nondegenerate semiconductor; b) degenerate semiconductor (the dashed curve is the Fermi function and the chain curve is the density of states).

of the high activation energy of this process. Using the obvious relationship  $N_a = N_0 + N_+$ , we find from Eq. (1.27) that the steady-state probability of the presence of a hole at an acceptor center is

$$p_0 = \frac{N_0}{N_a} = \frac{p}{p + \theta n + N_v \exp(-I_a/T)} = \frac{p}{p + \theta n} \frac{1}{1 + \exp[(\epsilon_1 - I_a)/T]}, \quad (1.28)$$

where  $\theta = W_n/W_p$  and

$$\epsilon_1 = T \ln \left( \frac{N_v}{p + \theta n} \right). \quad (1.29)$$

It follows from Eq. (1.28) that we cannot introduce a single quasi-Fermi level of free and localized holes, since the density of the latter  $N_0$  depends strongly on the value of  $\theta n$ . The carrier distribution is of quasi-equilibrium nature only in the case of shallow centers acting as traps, which are characterized by a time constant of thermal release of a carrier to a band  $\nu_T^{-1}$  shorter than the recombination time.<sup>55</sup> However, in the case of recombination centers which—by definition—obey the opposite condition, introduction of a quasi-Fermi level is clearly unjustified. We finally obtain the following expression from Eqs. (1.26) and (1.28):

$$R_{c,a} = 64\pi A (N_a a_h^3) n p \left[ p + \theta n + N_v \exp\left(-\frac{I_a}{T}\right) \right]^{-1}. \quad (1.30)$$

### e) Interimpurity (donor-acceptor) recombination

A real semiconductor always contains both acceptor and donor impurities, which usually act as traps of nonequilibrium carriers. At low temperatures, when the thermal release even from shallow impurity levels is a negligible process, the dominant effect is the interimpurity recombination process involving transitions of electrons captured by donors to one of the neighboring neutral acceptors. The distance between a donor and an acceptor not only governs the transition probability  $w_{d,a}$  given by Eq. (1.5) but also the energy of the emitted photon.<sup>41,56-59</sup> Then, in view of the discrete distribution of impurities in the lattice, line luminescence spectra are observed.<sup>60,61</sup> When the recombination takes place between electrons and holes captured by shallow impurities, the luminescence spectrum is in fact continuous,<sup>56,58,61</sup> since impurities that govern the luminescence energy near the spectral maximum are separated by a distance  $r$ , which is considerably greater than the lattice constant. In this case the energy of an emitted photon is<sup>56,58</sup>

$$\omega = E_g - I_a - I_d + E(r), \quad (1.31)$$

where  $E(r) \approx e^2/\epsilon r$ ; here  $I_a$  and  $I_d$  are the ionization energies of single acceptors and donors, and  $E(r)$  describes the Coulomb interaction between impurity ions

and carriers localized at these ions. In considering the luminescence spectrum we may assume that shallow impurities are distributed at random in a semiconductor. In fact, the correlation in the distribution of impurities is important only over distances such that the Coulomb energy of the interaction between impurities is comparable with the thermal energy corresponding to the freezing of the diffusion of impurities in the lattice. For realistic parameters of a semiconductor the correlation radius is approximately equal to the lattice constant,<sup>56,61</sup> and a pair of shallow impurities with such a short internal separation does not have any bound state.<sup>56,58</sup> We can thus see that the spectral intensity of the luminescence can be written in the form<sup>58,59,62</sup>

$$\Phi_{d,a}(\omega) = 4\pi\omega^2 N_d N_a r^2 w_{d,a}(r) \rho(r) \frac{dr}{d\omega} \sim r^4 p(r) \exp\left(-\frac{2r}{a_c}\right), \quad (1.32)$$

where  $\rho(r)$  is the average (over the impurity configurations) nominal probability of finding an electron at a donor if this donor is separated by a distance  $r$  from an acceptor with a localized hole.

In the case of a  $p$ -type semiconductor ( $N_a \gg N_d$ ) each donor is surrounded by a large number of neutral acceptors located at a distance  $r_i$  from the donor so that the quantity  $\rho(r)$  is governed only by the probability of occupancy of a specific donor.<sup>58</sup> This quantity satisfies<sup>62</sup> the equation<sup>61</sup>

$$\frac{\partial \rho}{\partial r} = -\rho \bar{\nu} + n(1-\rho)W_n + \nu_d(T)\rho, \quad (1.33)$$

where  $W_n$  is the electron-capture coefficient of a donor and  $\nu_d(T)$  is the probability of thermal release of an electron from a donor to the conduction band, which—applying the principle of detailed balance, as in the case of Eq. (1.27)—can be written in the form  $\nu_d(T) = W_n N_c \exp(-I_d/T)$ . The probability of a radiative transition of an electron to any acceptor  $\bar{\nu} = \sum_i \nu(r_i)$  is governed by the specific configuration of acceptors surrounding a given donor and, therefore, should be regarded as a random quantity. However, in considering the steady-state spectra we can replace  $\bar{\nu}$  with its average value<sup>62</sup>:

$$\bar{\nu} = \int w_{d,a}(r) \cdot 4\pi N_a r^2 dr = 4\pi N_a \int_0^\infty r^2 \exp\left(-\frac{2r}{a_c}\right) dr = 64\pi A N_a a_h^3. \quad (1.34)$$

It then follows from Eqs. (1.5) and (1.31)–(1.33) that, under steady-state conditions,<sup>62</sup>

$$\Phi_{d,a}(\omega) = 4\pi\omega N_a N_d \left(\frac{e^2}{\epsilon}\right)^3 \frac{nW_n \nu_d \exp(-4I_d'/E)}{\nu_d \exp(-4I_d'/E) + \bar{\nu} + \nu_d(T) + nW_n}, \quad (1.35)$$

where  $I_d' \approx I_d$ . It is clear from Eq. (1.35) that the energy at the maximum in the luminescence spectrum  $\omega_m$  corresponds to the excess photon energy  $E(r) = E_m$  of Eq. (1.31) described by

$$E_m = I_d \frac{\bar{\nu} + nW_n + N_c W_n \exp(-I_d/T)}{\nu_d \exp(-4I_d'/E_m) + \bar{\nu} + nW_n + N_c W_n \exp(-I_d/T)}, \quad (1.36)$$

and the donor-acceptor recombination rate is approximately

$$R_{d,a} = \frac{1}{\omega} \int_0^\infty \Phi_{d,a}(E) dE \approx \frac{64\pi A N_d (N_a a_h^3) n W_n}{64\pi A (N_a a_h^3) + nW_n + N_c W_n \exp(-I_d/T)}. \quad (1.37)$$

<sup>62</sup> See Footnote 5.

It is clear from Eqs. (1.34)–(1.36) that at low temperatures and low pumping rates the value of  $E_m$  and, consequently, that of  $\omega_m$  given by Eq. (1.31) is minimal. The lower the concentration  $N_a$ , the closer is the value of  $\omega_m$  to  $E_g - I_a - I_d$  (Refs. 59 and 60). When temperature and pumping rate  $J$  ( $n \propto J$ —Refs. 62 and 63) are increased, the value of  $\omega_m$  rises approaching  $E_g - I_a$ , i.e.,

$$E_g - I_a - I_d < \omega_m < E_g - I_a. \quad (1.38)$$

Dependences of this type are well supported by the experimental results<sup>63–69</sup> and they occur because on increase in  $J$  the pairs with large internal distances (“long-lived configurations”) responsible for the emission of the long-wavelength photons described by Eq. (1.31) become saturated faster because of the lower probability given by Eq. (1.5) and representing the relevant interimpurity transitions. Consequently, the luminescence begins to be dominated by pairs with shorter internal distances and this increases  $\omega_m$ . It follows from Eq. (1.35) that the spectral band profile and its intensity at saturating pumping rates are independent of  $T$  (Refs. 56, 58, and 61), in agreement with the experimental results.<sup>56,64</sup> At low pumping rates the thermal redistribution of electrons, via the band, from the long-lived to the short-lived configurations becomes important. Consequently, an increase in  $T$  reduces the intensity at the long-wavelength edge and increases somewhat the short-wavelength part of the spectrum. These features of the luminescence spectra are in agreement with the experimental results on  $p$ -type GaAs (Refs. 65–67).

The existence of configurations with different deexcitation times is manifested by certain features of the changes in the luminescence spectrum with time.<sup>56,62,68</sup> The intensity decreases much faster at shorter than at longer wavelengths and, therefore, long times correspond to smaller values of  $\omega_m$  (Refs. 18 and 67). This is due to the fact that after a time the recombination process begins to be governed by the long-lived configurations.<sup>56,64</sup> Thermal release of electrons from the long-lived configurations results in a narrowing of the spectrum with time.<sup>18,67</sup> The total intensity decreases in accordance with an essentially nonexponential law: at first the short-lived configurations are deexcited faster and an exponential decay corresponding to  $\nu_d(T)$  is established only after a longer time.

We shall now note some features of the interimpurity recombination process in strongly compensated samples for which the spectral intensity of the luminescence is calculated in Refs. 62 and 70. The condition  $N_a \approx N_d$  allows us to consider only the donor-acceptor pairs with the shortest internal distances,<sup>63,69</sup> and if the Bohr radius of a hole obeys  $a_h < a_c$ , we can assume that the hole is first captured by a pair. In fact, if the internal distance of a pair is  $r \leq 2a_c$ , a bound electron state does not exist at all,<sup>56,58</sup> and in the case of longer internal distances the process of thermal ionization results in the release of an electron to a band before recombination. In the photon energy range  $\omega = E_g - I_a$  corresponding to pairs with  $r \approx 2a_h$ , the smallness of  $I_d(r)$  has the effect that the thermal release of holes to

the valence band is important and this results in thermal quenching of the short-wavelength luminescence edge.<sup>72</sup> It should be noted that the long-wavelength edge of the spectrum is governed by transitions between donors and acceptors separated by large distances, in accordance with Eq. (1.31). The probabilities (1.5) of such transitions are low and, consequently, the intensity at the long-wavelength edge decreases as a result of an increase in  $T$  because of the thermal release of electrons to the band, exactly as in the case of a  $p$ -type semiconductor. In other respects the changes in the luminescence spectrum which occur as a result of changes in  $T$  and the rate of excitation are qualitatively the same as in the case of  $p$ -type semiconductors. However, the spectral changes in the case considered can be quite large.<sup>62</sup>

In the case of strongly compensated semiconductors the termination of excitation is followed by decay not only of the donor occupancy but also of the acceptor occupancy. This slows down the decay of the luminescence intensity.<sup>72</sup> In fact, if  $t > \nu_d^{-1}(T)$ , all pairs with  $r$  such that  $\nu(r) > \nu d$  have already become deexcited. In the case of donor-acceptor pairs with large values of  $r$ , electrons and holes localized at them are released thermally to a band before recombining, i.e., electrons jump between donors until they are located at a distance from a localized hole such that  $\nu(r) \approx \nu_d(T)$ . Pairs with such a fixed value of  $r$  govern the luminescence, i.e.,  $\omega_m$  ceases to depend on time. The occupancies of donors and acceptors then decay in accordance with the bimolecular law so that the total luminescence intensity obeys  $\Phi_{d,a} \propto t^{-2}$ . Such decay of  $\Phi_{d,a}(t)$  is a characteristic feature of strongly compensated semiconductors at low temperatures.<sup>56,57</sup>

#### f) Role of different radiative recombination channels

We shall stress particularly that the role of a given recombination channel is governed not so much by the probability of the corresponding radiative transition (Sec. 1 a) as by the nature of the distribution of carriers between the energy levels. At low temperatures the luminescence emitted from pure crystals is mainly due to the exciton recombination process.<sup>45–47</sup> In the case of a doped semiconductor (for example, one with  $n$ -type conduction) the role of this recombination is governed by the ratio of the capture time of a hole by an acceptor to the time that a hole is bound to an electron to form an exciton.<sup>74</sup> If  $N_a \gg n$ , then the interimpurity recombination predominates because practically all the nonequilibrium carriers are trapped by the impurity centers involved. When temperature is increased, thermal release of electrons to the band becomes important and  $\omega_m$  approaches  $E_g - I_a$  in accordance with Eq. (1.38). This quantity is typical also of the impurity recombination case [Eq. (1.24)] whose role increases continuously as temperature is increased. Thus, in a certain range of temperatures the interimpurity and impurity recombination mechanisms determine the luminescence in the same frequency range. We can identify the dominant channel only on the basis of the shape of the luminescence spectrum and its time characteristics. A comparison of Eqs. (1.30) and (1.37)

shows that the temperature from which the impurity recombination predominates is less than the ionization energy of a donor level. According to the experimental results,<sup>18</sup> in the case of GaAs characterized by  $I_d \approx 6$  meV ( $\approx 70^\circ\text{K}$ ), the impurity recombination process becomes significant already at  $T \approx 15\text{--}20^\circ\text{K}$ . The role of the impurity recombination increases on increase in the rate of excitation. In the interpretation of the spectra of the impurity and interimpurity luminescence<sup>18</sup> one should allow for the possibility of recombination of an electron with a hole, which is in an excited acceptor state.<sup>40,73</sup> Further increase in temperature results in quenching of the impurity luminescence which is then mainly due to the interband recombination process whose characteristic time is minimal when electrons or holes are degenerate [Eq. (1.19)]. However, at high carrier densities we can expect new nonradiative recombination channels: Auger (impact)<sup>75</sup> and plasma.<sup>76</sup>

## 2. LUMINESCENCE OF HEAVILY DOPED SEMICONDUCTORS

The radiative recombination process in heavily doped semiconductors is fairly complex because of the special features of the energy spectra of these semiconductors and also because of the distribution of carriers between the states. The energy spectrum of a heavily doped semiconductor is treated in detail in Refs. 27 and 28. In Sec. 2a we shall give only the basic information required in the subsequent discussion. Next, we shall identify the main radiative recombination channels in heavily doped semiconductors and we shall discuss each of them in the subsequent subsections (Secs. 2b–d). At the end of Sec. 2a we shall discuss the most typical experimental situations and for each case we shall identify the dominant radiative recombination channels. We shall deal specifically with the case of a heavily doped and strongly compensated semiconductor in Sec. 2e. Finally, in Sec. 2f we shall discuss the special features of the transient characteristics of the luminescence emitted by heavily doped semiconductors.

### a) Energy spectrum of heavily doped semiconductors. Main radiative recombination channels

Heavily doped semiconductors are those in which the average distance between impurities is less than the Bohr radius of an impurity state. In the case of an  $n$ -type semiconductor there are no localized states corresponding to single donors if the heavy doping condition  $N_d a_c^3 > 1$  is satisfied ( $N_d$  is the donor concentration and  $a_c$  is the Bohr radius of a donor state). In fact, if  $N_d a_c^3 > 1$ , the kinetic energy of an electron localized in a region of size  $r_s \approx N_d^{-1/3}$  (equal to the average distance between donors) is higher than the energy of the Coulomb attraction by a donor. An impurity level is then displaced to a band and the semiconductor becomes degenerate. For this reason a heavily doped semiconductor does not contain excitons and, consequently, it is meaningless to talk of exciton luminescence.

The heavy doping condition also means that the screening radius  $r_0$  of the Coulomb potential is less than the Bohr radius  $a_c$ , i. e.,

$$r_0 = \left(\frac{\pi}{3}\right)^{1/6} \left(\frac{a_c}{4\pi^{1/2}}\right)^{1/2} \approx \frac{1}{2} a_c (n a_c^3)^{-1/6} < a_c. \quad (2.1)$$

The effective electron mass  $m_c$  is small in some semiconductors so that the condition  $N_d a_c^3 > 1$  is obeyed only in the case of relatively low donor concentrations: for example, in the case of InSb this happens for  $N_d > 10^{14}$   $\text{cm}^{-3}$ , whereas for GaAs it occurs beginning from  $N_d \approx 5 \times 10^{17}$   $\text{cm}^{-3}$ . The donor concentrations in radiative  $p$ - $n$  structures are usually higher than these values.

In heavily doped semiconductors the state of an electron is governed not so much by the field of a single impurity as by the field created by all the impurities and carriers present in a given semiconductor. This many-body interaction results in broadening of an impurity level, i. e., it produces an impurity band and considerable density-of-states tails in the band gap. These tails appear in the presence of any random field.<sup>28</sup> The field may be associated with macroscopic inhomogeneities of a sample, thermal vibrations of the lattice which are the cause of the Urbach tails (Sec. 1c), and fluctuations of the charge in an electron-hole plasma created, in particular, by external excitation.

Reliable theoretical results on the energy spectrum and the nature of electron states in a degenerate heavily doped semiconductor have been obtained for energies close to the Fermi level  $F_n$  as well as for energies corresponding to strongly localized states (see, however, Ref. 77). In fact, electrons near the Fermi level have a high kinetic energy  $\mu_n = F_n - E_c = (\hbar^2/m_c) N_d^{2/3}$  and this energy is considerably greater than the potential energy of the interaction between electrons themselves and also between electrons and impurities ( $e^2/\epsilon) N_d^{2/3}$  ( $\epsilon$  is the permittivity). Consequently, near these energies the electron gas is only slightly nonideal. The theory of a Fermi gas with a weak interaction was developed back in the thirties,<sup>78</sup> and the results can be found in books.<sup>79</sup> The influence of the Coulomb interaction reduces to an increase in the effective mass of carriers and a reduction in the Fermi energy: the dispersion law and the nature of the wave functions at energies close to  $F_n$  remain practically the same as for an ideal crystal.

At energies close to the bottom of the conduction band  $E_c^0$  of an unperturbed crystal the kinetic energy of electrons is low and the interaction of electrons with one another and with impurities becomes predominant. The strong scattering of electrons makes it impossible to describe their states by the Bloch function, i. e., in this range of energies the wave vector  $k$  is a good quantum number and it is pointless to talk of the dispersion law. A convenient characteristic of the energy spectrum of a heavily doped semiconductor is the density of states  $\rho(\epsilon)$ . This function does not vanish at energies corresponding to the edge of the unperturbed conduction band ( $E_c^0$ ) but forms a tail of the density of states (Fig. 6a). The edge of the valence band spreads in a similar manner. The electron states at energies  $E < E_c^0$  are associated with random clusters of several donors, i. e., with local fluctuations of the donor concentration. The characteristic size of a potential well which appears because of the random distribution of impurities is equal to the screening radius  $r_0$  of Eq. (2.1) and its

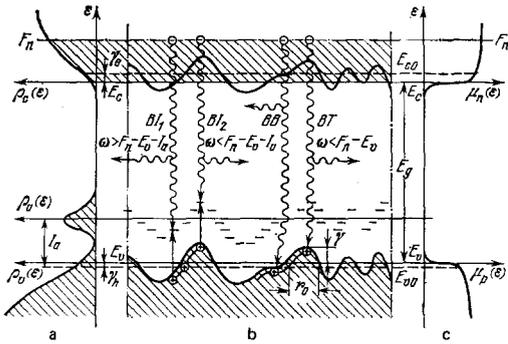


FIG. 6. Energy band diagram and radiative recombination channels of a degenerate heavily doped semiconductor: a) density of states  $\rho(\epsilon)$ ; b) local distortion of the band edges due to fluctuations of the impurity potential; c) electron  $\mu_n$  and hole  $\mu_p$  mobilities ( $E_c$  and  $E_v$  are the percolation levels of electrons and holes;  $\rho_a$  is the density of states near the acceptor level with an ionization energy  $I_a$ ). The wavy lines represent the following channels: band-tail (BT) transitions, band-band (BB) transitions, and band-impurity (BI) transitions.

rms depth is<sup>25-28</sup>

$$\gamma = \sqrt{2\pi} \frac{e^2}{\epsilon r_0} \sqrt{N_d r_0^3} \quad (2.2)$$

In fact,<sup>27</sup> the rms fluctuation of the number of impurities in a volume of size  $r_0$  is of the order of  $\sqrt{(4\pi/3)N_d r_0^3}$  and the potential energy of an electron in the field of such a fluctuation is  $(e^2/\epsilon r_0)\sqrt{(4\pi/3)N_d r_0^3} \approx \gamma$ .

If an  $n$ -type heavily doped semiconductor contains only donors, the density-of-states tail of the valence band differs from the corresponding tail of the conduction band by being sharply restricted.<sup>27</sup> The deep acceptor states now occur in the parts of a crystal where there are no donors whatever. However, in practice all the heavily doped semiconductors are compensated,<sup>7)</sup> so that we shall concentrate specifically on compensated materials. In the case of a compensated  $n$ -type heavily doped semiconductor the density-of-states tail  $\rho_v(E_h)$  of the valence band penetrates without restriction into the band gap. The probability of small fluctuations of the potential is given by the Gaussian distribution. Therefore, if we regard a hole as a classical particle, we find that  $\rho_v(E_h)$  in the range  $E_h > E_v$  is a Gaussian function<sup>27</sup> with the variance described by Eq. (2.2), where  $N_d$  is replaced with  $N = N_d + N_a$ . The states lying deep within the band gap are formed as a result of clustering of several acceptors in a region of size  $r < r_0$ . When the number of impurities in a cluster is considerably greater than unity, each such cluster can be regarded<sup>27</sup> as a uniformly charged sphere of radius  $r$ . The form of  $\rho_v(\epsilon)$  can then be obtained from the following simple considerations. The probability  $Q$  that  $z$  impurities of the same sign are located in a region where on the average there are  $m$  impurities is given by the Poisson formula, which can be written in the

<sup>7)</sup> The absorption and luminescence spectra of some heavily doped semiconductors, particularly Sn-doped InAs and GaAs (Ref. 83), indicate that very short tails are formed and this is clearly associated with a low degree of compensation governed by the individual properties of the impurity used and by the conditions during the preparation of the samples.

following form if  $z > 3$ :

$$Q = \exp \left[ z \ln \left( \frac{m}{z} + 1 \right) \right].$$

The deep states under consideration are hydrogen-like,<sup>27</sup> so that  $z \approx \sqrt{\epsilon/I_a}$  and we approximately find that

$$\rho(\epsilon) = \rho_0 \exp \left( -\sqrt{\frac{\epsilon}{I_a}} \ln \sqrt{\frac{\epsilon}{I_a}} \right).$$

More exact formulas allowing for the finite size of a cluster of impurities and for the Coulomb interaction between impurities are given in Refs. 27 and 28.

According to these formulas, the density of states in the valence band tail of a compensated heavily doped semiconductor can be written in the form

$$\rho_v(\epsilon) = \rho_0^s \exp \left[ -\left( \frac{\epsilon}{\gamma_{h,s}} \right)^s \right], \quad \epsilon = E_h - E_v > 0, \quad (2.3)$$

where

$$s=2, \quad \gamma_{h,2} = \sqrt{2} \gamma = (4\pi N r_0^3)^{1/2} \frac{e^2}{\epsilon r_0} \quad \text{for } 0 < \epsilon < E_{0h} = \gamma^{4/3} \gamma_{h,1/2}^{-1/2}, \quad (2.3a)$$

$$s=\frac{1}{2}, \quad \gamma_{h,1/2} = I_a \ln^{-2} \left[ \left( \frac{\epsilon}{I_a} \right)^2 \frac{D(\epsilon)}{N_a a_h^2} \right] \approx I_a D^{-4/3}(\gamma) \quad \text{for } E_{0h} < \epsilon < E_{1h}, \quad (2.3b)$$

$$s=\frac{3}{2}, \quad \gamma_{h,3/2} = (\lambda I_a T_0^2)^{1/3} \quad \text{for } \epsilon > E_{1h} = \lambda^{1/2} T_0 \ln \left[ \left( \frac{T_0}{I_a} \right)^2 \frac{D_h(T_0)}{N_a a_h^2} \right]. \quad (2.3c)$$

Here,

$$D_h(\epsilon) = \ln^{3/2} \left[ \left( \frac{\epsilon}{I_a} \right)^2 (N_a a_h^2)^{-1} \right],$$

$\lambda$  is of the order of unity, and  $T_0$  is the temperature of "freezeout" of impurities in the lattice.<sup>27,28</sup> The formulas (2.3) describe  $\rho_v(\epsilon)$  only approximately. In fact,<sup>27</sup> they are derived as asymptotic forms and are used only in a limited range of energies; in real situations the values of  $\gamma$ ,  $E_{0h}$ , and  $E_{1h}$  do not differ greatly. Therefore, it is frequently possible to use the simple approximation<sup>7,18</sup> described by  $\rho_v(\epsilon) \propto \exp(-\epsilon/\gamma_0)$ , where  $I_a < \gamma_0 < \gamma$ .

The formulas (2.3) describe qualitatively also the density-of-states tail of the conduction band. In Eqs. (2.3b)–(2.3c) the quantities referring to acceptors should be replaced with the donor parameters. There are doubts about the validity of Eq. (2.3a) in most cases. This is due to the following reasons: the formula (2.3a) is derived using a quasiclassical approximation which is justified usually for holes of greater effective mass than electrons. In the case of small values of  $m_c$  the ground energy level of an electron in a potential well is located considerably above the bottom of the well. This can be allowed for if we use Eq. (2.3a) with  $\gamma_{c,2} < \gamma_{h,2}$  (see the end of Sec. 2b).

It should be stressed that fairly deep states in the tail resemble impurity rather than band states, i.e., they are strongly localized in the sense that the conductivity (mobility) involving these states is close to zero.<sup>89-94</sup> In the case of shallower states the mobility increases abruptly at energies  $E_c$  and  $E_v$ , which are called the percolation levels of electrons and holes, respectively. In other words, the mobility  $\mu$  considered as a function of the carrier energy has a definite gap  $E_c - E_v$  (Fig. 6c). Similar considerations are usually employed in discussing amorphous semiconductors.<sup>24,28,89,94</sup> It should be noted that the percolation level  $E_v$  (Fig. 6),

above which holes can be regarded as mobile (free), differs from the energy  $E_v^0$  corresponding to the top of the valence band of an undoped semiconductor and the difference is  $\gamma_h \approx (2/3)\gamma$  (Refs. 93 and 89). If  $m_e \ll m_h$ , the quantity  $\gamma_e = E_c^0 - E_c$  (Fig. 6) can be considerably greater. The band gap of a heavily doped semiconductor can naturally be described by

$$E_g = E_c - E_v - \Delta E_g = E_g^0 - \gamma_e - \gamma_h - \frac{e^2}{\epsilon r_0} - \frac{2e^2}{\epsilon} n^{1/3}, \quad (2.4)$$

where  $\Delta E_g$  (the last two terms) describes the carrier-density narrowing of the band resulting from the interaction of recombining electrons and holes with carriers already present in a semiconductor<sup>80,88</sup> (see Sec. 1 c).

We shall now identify the three main types of radiative transition in a heavily doped semiconductor and we shall consider which of them predominate in a given experimental situation. We shall consider only the case when  $m_e \ll m_h$ . When this condition is valid, the theory simplifies greatly and becomes clearer. Moreover, the condition is satisfied by a large margin in the case of the direct-gap semiconductors GaAs, InSb, and InAs which have been investigated more than the others. We shall compare the theory and experiment for these specific semiconductors.

We shall assume that a compensated heavily doped semiconductor satisfies the condition  $N_d a_0^3 > 1$ . Then, bearing in mind that  $a_e \gg a_h$  we have to distinguish the case of: a) intermediate doping ( $N_d a_0^3 > 1$  but  $N_a a_0^3 < 1$ ); b) heavy doping with acceptors ( $N_a a_0^3 > 1$ ). In case a) there are localized states linked to single acceptors, i.e., we can expect  $\rho_v(\epsilon)$  to have a maximum at  $\epsilon = I_a$  (Fig. 6a). However, it should be noted that such a maximum does not appear if even in the case of moderate doping we have  $\gamma > I_a$  (Ref. 27). This situation should also be regarded as case b), when the density-of-states tails decrease monotonically with depth in the band.

In the case of an  $n$ -type heavily doped semiconductor the density-of-states tail has practically no influence on the absorption<sup>27</sup> and luminescence<sup>29</sup> spectra. Recombination radiation in the region of a spectral maximum is due to electron transitions from levels lying close to  $F_n$ , i.e., far from the free band (Fig. 6). On the other hand, the density-of-states tail of the valence band has a considerable influence on the luminescence spectrum because nonequilibrium holes are first captured in localized "tail" states and then they recombine with electrons.<sup>29,31</sup> Therefore, when case a) applies, the luminescence is governed by the recombination of free electrons with holes localized at acceptor levels ( $BI$  transitions in Fig. 6) and at deep ( $E_h > E_v$ ) tail levels ( $BT$  transitions), and also with free holes ( $BB$  transitions). In case b) or, more exactly, when there is no maximum of  $\rho_v(\epsilon)$  at  $\epsilon = I_a$ , luminescence is governed by the  $BT$  and  $BB$  transitions. These are important only at high temperatures or low pumping rates. The luminescence corresponding to such transitions is in fact considered in Sec. 1 c. The luminescence spectrum due to  $BT$  transitions is considered in Sec. 2 b and that due to  $BI$  transitions is discussed in Sec. 2 c.

In the case of  $p$ -type heavily doped semiconductors we

have to allow for the capture of nonequilibrium electrons by localized states in the conduction band tail. Thus, for these materials in case a) luminescence is governed not only by  $BB$ ,  $BT$ , and  $BI$  transitions, but also by  $TI$  and  $TT$  transitions (see Fig. 13 below), which correspond to the recombination of electrons trapped by deep states in the conduction band tail with holes localized correspondingly at acceptors in deep states of the valence band tail. The luminescence emitted in this case is considered in Sec. 2 d, where attention is concentrated mainly on  $TI$  transitions (interimpurity radiative recombination).

In case b), i.e., in degenerate  $p$ -type heavily doped semiconductors the luminescence is governed by  $BB$  and  $BT$  transitions, exactly as in the case of  $n$ -type heavily doped semiconductors. The differences which follow from the inequality  $m_e \ll m_h$  are discussed at the end of Sec. 2 b.

In Sec. 2 e we shall consider separately the luminescence emitted by strongly compensated heavily doped semiconductors. For these materials the value of  $\gamma$  is particularly large and, as a rule, we have case b). Nonequilibrium electrons and holes in these semiconductors fill the tail states, so that  $TT$  transitions play an important role.

## b) Interband radiative recombination in heavily doped semiconductors

In the case of a degenerate  $n$ -type heavily doped semiconductor the energy of a hole is governed by the local fluctuations of the impurity potential, and the position of the Fermi level of electrons  $F_n$  is the same for the whole crystal (Fig. 6). Consequently, the characteristic energy of the photons emitted as a result of recombination varies from point to point in such a crystal. This determines the position of the maximum and the profile of the luminescence line. It is important to note that, in spite of the continuous energy spectrum of a heavily doped semiconductor, the distribution of nonequilibrium holes in the tail states cannot be regarded as quasiequilibrium *a priori*,<sup>29,30</sup> i.e., it cannot be described by a quasi-Fermi level (this is usually true of free holes; see Sec. 1 c). In fact, the continuity of  $\rho_v(\epsilon)$  represents only the average over the whole volume of a crystal. Levels form in the band gap at different points in a crystal because of clustering of several acceptors or, more exactly, because of local fluctuations of the impurity potential (Fig. 6). We can thus see that states in the valence band tail with energies  $E_h > E_v$  can be regarded in a natural manner as a set of acceptor levels. As shown in the theory of heavily doped semiconductors,<sup>27</sup> each energy in the tail corresponds to a fluctuation-induced potential well of specific size (optimal fluctuations). For example, in the region of small (Gaussian) fluctuations we have  $R = r_0$ , whereas for deeper states we obtain  $R < r_0$ . This allows us to assume the potential wells to be smooth without additional minima, which is confirmed also by the monotonic nature of the correlation function of the fluctuations of the potential.<sup>27,30</sup> Fairly deep potential wells corresponding to localized states ( $E_h > E$ ) are separa-

ted from one another by fairly large distances, which are greater than the characteristic size of a well  $R$ . This means that the overlap of the wave functions of holes localized even in neighboring wells is exponentially small because of the relatively large value of  $m_h$  (Ref. 92). In other words, each potential well of this kind resembles a single impurity center.

In discussing the recombination of holes localized in the tail states we need allow only for the ground state in each fluctuation well,<sup>8)</sup> since excited states correspond to the same energies as the ground states in shallower wells, but the number of such wells is considerably greater. For this reason the tail density of states has been calculated allowing only for the ground states.<sup>28,27</sup> It follows from these representations that the probability of an "acceptor" well with an ionization energy  $\varepsilon = E_h - E_v > 0$  satisfies an equation<sup>29</sup> similar to Eq. (1.27):<sup>9)</sup>

$$\frac{\partial q_h(\varepsilon)}{\partial t} = pW_p(\varepsilon)(1 - q_h) - n\tilde{W}_n(\varepsilon)q_h - W_p(\varepsilon)N_v \exp\left(-\frac{\varepsilon}{T}\right)q_h, \quad (2.5)$$

where  $n$  and  $p$  are the densities of free electrons and holes;  $W_p$  is the coefficient of the capture of a free hole by an "acceptor" well of this kind, which depends weakly (as a power law) on the depth of the well and on temperature<sup>95,96</sup>;  $\tilde{W}_n$  is the coefficient representing radiative recombination of a free electron and a localized hole of energy  $E_h$ ;  $N_v$  is the effective number of nonlocalized states (with energies  $E_h < E_v$ ) in the valence band of a heavily doped semiconductor. The last term in Eq. (2.5) allows for the thermal release of a hole from an "acceptor" well to the valence band, i.e., to nonlocalized states. Equation (2.5) ignores the tunnel transitions of holes between the wells because, as pointed out earlier, the probability of such transitions is exponentially small<sup>89,92</sup> and it can be ignored compared with the probabilities of recombination of a hole and its transfer to a band (this is at least true for  $m_h \gg m_c$ ).

Under steady-state conditions, we find that Eq. (2.5) gives

$$q_h(\varepsilon) = \frac{pW_p}{pW_p + n\tilde{W}_n + W_pN_v \exp\left(-\frac{\varepsilon}{T}\right)} = \frac{p}{p + \theta n} \left[ 1 + \exp\left(\frac{\varepsilon_p - \varepsilon}{T}\right) \right]^{-1}, \quad (2.6)$$

where

$$\varepsilon_p = T \ln \left( \frac{N_v}{p + n\theta(\varepsilon)} \right), \quad \theta(\varepsilon) = \frac{\tilde{W}_n(\varepsilon)}{W_p}. \quad (2.6a)$$

The formula (2.6) is analogous in meaning to Eq. (1.28) and it shows that the distribution of holes between localized tail states is very different from the quasiequilibrium function. Thus, if the distribution of holes is described by a quasi-Fermi level  $F_p$ , then at  $T=0$  all the states with  $E_h < F_p$  would be occupied by holes and the states with  $E_h > F_p$  would be free. In fact, it follows from Eq. (2.6) that at  $T=0$  the localized states are occupied by holes and the probabilities of occupancy are similar for these states: these probabilities differ considerably from unity and are given by  $p(p + \theta n)^{-1}$ . In

<sup>8)</sup> Just as above, only the ground state of the acceptor is taken into account in the theory of impurity recombination.<sup>54</sup>

<sup>9)</sup> See Footnote 5 and the remark at the end of this subsection.

fact, a free hole captured by a localized tail state at  $T=0$  is more likely to recombine with one of the free electrons than to go over to a different localized state because the overlap of the wave functions of holes in localized states is very small. The degree of occupancy of each localized state is governed by the rates of capture of holes and of the recombination of these holes with electrons. Therefore, the higher the value of  $n$ , the greater the rate of recombination of electrons with localized holes and the smaller the degree of occupancy of each state. When temperature is increased, the thermal release of holes from localized states becomes important and, therefore, the degree of occupancy of shallow wells (with energies close to  $E_v$ ) decreases, whereas the occupancy of deeper wells increases.

The situation described here is well known in the theory of impurity recombination when luminescent impurity centers are divided arbitrarily into trapping and recombination centers. By definition,<sup>55</sup> the trapping levels obey the condition that the time for thermal release from these levels is less than the recombination time and, therefore, the distribution of carriers between such levels is of quasiequilibrium type. The opposite condition is satisfied by the recombination levels (centers) so that the distribution of carriers between them cannot be described by introducing a quasi-Fermi level. It follows from Eq. (2.6) that the tail states with ionization energies lower than  $\varepsilon_p^0 = \varepsilon_p(\varepsilon_p^0)$  act as the trapping levels, whereas the states with  $\varepsilon > \varepsilon_p^0$  act as the recombination levels. In other words,  $\varepsilon_p^0$  is the demarcation level separating the localized states in the tail into these two types. Naturally, at temperatures  $T > \gamma$  the demarcation boundary separating the recombination and trapping levels becomes broader and the distribution of holes becomes practically quasiequilibrium. However, it should be noted that at temperatures  $T > \gamma$  the majority of the states localized in the tails is empty because of the thermal release of carriers and the luminescence is mainly due to the radiative recombination of free (BB channel) and not of localized (BT channel) holes (Fig. 6).

The fact that the experimental results obtained in investigations of the static and transient characteristics of the luminescence of compensated heavily doped semiconductors are in conflict with the assumption of a quasiequilibrium distribution of carriers between the tail states has been pointed out by the authors of experimental papers of Refs. 90, 97, 98.

If we know the distribution of holes between the localized tail states, given by Eq. (2.6), we can calculate the spectral intensity of the luminescence due to the BT transitions (Fig. 6) from

$$\Phi_{BT}(\omega) = \omega \int \int W_{BT}(E_c, E_h) \rho_c(E_c) f_c(E_c) \rho_v(E_h) q_h(E_h) \delta(E_c - E_h - \omega) dE_c dE_h, \quad (2.7)$$

where  $W_{BT}(E_c, E_h)$  is the coefficient of radiative recombination of a free electron of energy  $E_c$  and a localized hole of energy  $E_h > E_v$ . Since we are considering free

electrons, their distribution is of the quasiequilibrium type, i. e.,  $f_e(E_c)$  is the Fermi function. The density of states  $\rho_c(E_c)$  can be described by the usual expression (1.21), since the corrections associated with heavy doping are small at energies  $E_c \approx F_n$ , as pointed out in Sec. 2a, and the actual form of the density of states at energies  $E_c \leq E_c$  has little effect on the main results.

We shall now consider the dependence of  $W_{BT}$  on the energies of an electron  $E_c$  and a hole  $E_h$ . If the ground-state energy  $\varepsilon = E_h - E_v$  in an "acceptor" potential well (which represents a potential hump for electrons, see Fig. 6) is less than  $\mu_n = F_n - E_c$ , electrons approach a hole freely, so that  $W_{BT}$  is a weak (power-law) function of the carrier energy. Transitions of this kind correspond to photon energies  $\omega > E_g$  (Fig. 6). If a hole is localized in a deeper potential well ( $\varepsilon > \mu_n$ ), an electron may recombine with such a hole only by tunneling. Transitions of this kind are responsible for the luminescence in the photon energy range  $\omega < E_g$ . As pointed out earlier, deep states in the valence band tail are due to local clusters of a large number of acceptors. The number of acceptors in a cluster is governed by the well depth:  $Z_h = \varepsilon^{1/2} I_a^{-1/2}$ . In this case a potential hump for electrons represents a repulsive Coulomb center of charge  $-eZ_h$  screened at distances  $r > \tilde{r} = Z_h e^2 (\varepsilon \mu_n)^{-1}$  because of expulsion of free electrons from the region adjoining the cluster. Using the quasi-classical approximation, we obtain the interpolation formula<sup>31</sup>

$$W_{BT}(E_c, E_h) = W_{BT}^0 \exp\left(-2\pi \sqrt{\frac{m_e}{m_h} \frac{E_h - E_v}{E_c - E_c + \mu_n}}\right), \quad (2.8)$$

which reduces in the limit  $\mu_n \rightarrow 0$  to the familiar formula<sup>27, 28</sup> for an unscreened Coulomb center. The corresponding coefficient of radiative capture of electrons at temperatures  $T < \mu_n = F_n - E_c$  is

$$\tilde{W}_n(\varepsilon) = \frac{1}{n} \int_{E_c}^{\infty} \rho_c(E_c) f_e(E_c) W_{BT}(E_c, E_h) dE_c \approx \tilde{W}_n^0 \exp\left(-2\pi \sqrt{\frac{m_e}{m_h} \frac{\varepsilon}{\mu_n}}\right), \quad (2.9)$$

where

$$W_{BT}^0 = 64 A a_h^3 \sqrt{\frac{m_h (E_g - E_c)}{m_e I_a}} \frac{\varepsilon}{I_a}, \quad \tilde{W}_n^0 = \frac{64}{\pi} A a_h^3 \frac{m_h \mu_n}{m_e I_a}, \quad \varepsilon_0 = E_h - E_v.$$

Substituting in Eq. (2.7) the expressions (2.6) and (2.8), we find that the spectral intensity of the interband radiative recombination in compensated heavily doped semiconductors resulting from band-tail transitions (BT transitions; see Fig. 6b) is given by<sup>29, 31</sup>

$$\Phi_{BT}(\omega) = P \rho_v^0 W_{BT}^0 \times \int_{\max(E_g - \omega, 0)}^{\infty} d\varepsilon \frac{\rho_c(\omega - E_g + \varepsilon) \exp\left[-2\pi \sqrt{\frac{m_e}{m_h} \frac{\varepsilon}{\omega - E_g + \mu_n + \varepsilon - \left(\frac{\varepsilon}{\gamma_{h,s}}\right)^s}}\right]}{[p + n\theta(\varepsilon)] \left[1 + \exp\left(\frac{\varepsilon_p - \varepsilon}{T}\right)\right] \left[1 + \exp\left(\frac{\omega - E_g - \mu_n + \varepsilon}{T}\right)\right]}, \quad (2.10)$$

where  $s$  and  $\gamma_{h,s}$  are selected depending on which energy interval of Eq. (2.3) is  $\varepsilon$  located. Examples of the  $\Phi_{BT}(\omega)$  spectra plotted according to Eq. (2.10) and using numerical integration are shown in Figs. 3b and 7. The theoretical curves in Fig. 3b are compared with the experimental photoluminescence spectra<sup>52</sup> of InSb samples with different degrees of doping. The theory<sup>28, 29</sup> does not allow us to find accurately the values

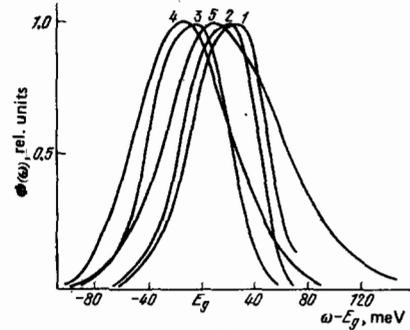


FIG. 7. Theoretical luminescence spectra of heavily doped semiconductors representing recombination of free electrons with holes localized in tail states (BT transitions, Fig. 6). The curves are calculated using Eq. (2.10) and assuming the parameters of GaAs:  $N_d \approx 10^{18} \text{ cm}^{-3}$ ,  $\mu_n = F_n - E_c = 70 \text{ meV}$ ,  $\gamma = 30 \text{ meV}$ , and  $\lambda = \ln[N_v / (p + \theta n)] = 7$ . Temperature ( $^{\circ}\text{K}$ ): 1) 4.2; 2) 40; 3) 77; 4) 150; 5) 300.

of  $\gamma_c$  and  $\gamma_h$  occurring in Eq. (2.4) for  $E_k$  and the value of  $E_k(n)$  determines the energy of the emitted photons [Eq. (2.10)]. Therefore, in plotting the curves in Fig. 3b it is assumed, in accordance with Eqs. (2.2) and (2.4), that  $E_k = E_k^0 - \alpha\sqrt{n}$ , and the coefficient  $\alpha$  is selected so that the position of the maxima of curves 2 and 2' coincide. It is clear from Fig. 3b that the theoretical curves plotted on this basis are in good agreement with the experimental results. This good agreement between the theory and experiment is largely explained by the fact that the effective mass of electrons in InSb is small and that  $m_h \gg m_e$ , i. e., the conditions used in the derivation of Eq. (2.10) are satisfied by a large margin. The curves in Fig. 7 illustrate the effects of increase in temperature on the luminescence spectrum. They are plotted using the parameters of GaAs with  $N_d \approx 10^{18} \text{ cm}^{-3}$ , i. e., with donor concentrations typical of electroluminescent structures. The calculated spectra (Fig. 7) are in qualitative agreement with those found experimentally.<sup>7, 18, 105, 134</sup> Unfortunately, it is not possible to carry out a quantitative comparison of the theory with experiment. This is due to the fact that in this case the parameter  $N_d a_c^3$  is of the order of unity and particularly, as stressed in the Introduction, throughout this review the densities of nonequilibrium carriers are assumed to be given. Under experimental conditions the density of nonequilibrium carriers (holes) created by photoexcitation or by injection depends strongly on the coordinate and temperature and the nature of such dependences is governed by the dominant recombination channel which is usually nonradiative.<sup>10</sup> The exception to this rule is the range of low temperatures, when according to Eq. (2.10) the shape of the spectrum is independent of the nonequilibrium carrier density.<sup>29</sup> This has made it possible to carry out a quantitative comparison for InSb (Fig. 3b).

It is clear from Fig. 7 that the interband lumines-

<sup>10</sup> This is the reason why also in the subsequent subsections we are comparing the theory with the experimental results only qualitatively, employing those dependences which manifest the main characteristic features of the investigated radiative recombination channel in heavily doped semiconductors.

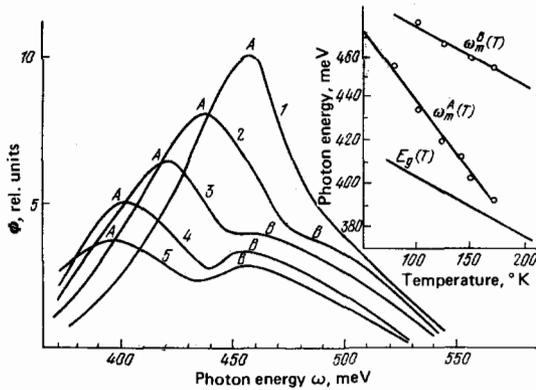


FIG. 8. Edge luminescence spectra of  $n$ -type InAs ( $n = 2 \times 10^{18} \text{ cm}^{-3}$ ) obtained<sup>99</sup> at various temperatures  $T$  ( $^{\circ}\text{K}$ ): 1) 77; 2) 100; 3) 123; 4) 150; 5) 170. The inset shows the temperature dependences of the band gap  $E_g$  of indium arsenide and of the spectral maxima  $A$  and  $B$ .

cence spectrum of a heavily doped semiconductor does not terminate at  $\omega = E_g$ , as suggested by Eq. (1.18), but decreases toward longer wavelengths in accordance with approximately the same law as  $\rho_v(\epsilon)$ . The quantity  $\gamma_{h,s}$  is a characteristic energy of this fall also on the short-wavelength side, whereas according to Eq. (1.18) this should be the quantity  $T$  (Fig. 3a). These conclusions can also be obtained from rough estimates<sup>29</sup> of the integral in Eq. (2.10), which indicate that at low temperatures the energy of the spectral maximum is

$$\omega_m \approx E_g + \mu_n - \sqrt{2} \gamma - \epsilon_p^0 \quad \text{for} \quad \epsilon_p^0 < E_{oh}, \quad \frac{\gamma^2}{T}. \quad (2.11)$$

This result is readily understood if we bear in mind the physical meaning of the quantity  $\epsilon_p^0$ . In fact, in discussing the distribution (2.6), we have mentioned that  $\epsilon_p^0$  gives the position of the demarcation level separating localized states in the tail into recombination and trapping levels, emptied by thermal ionization. This means that  $\epsilon_p^0$  is the characteristic energy of ionization of the acceptor levels which at a given temperature determine radiative recombination and, therefore, Eq. (2.11) follows in fact from Eq. (1.25) if  $I_a \approx \epsilon_p^0$  is substituted in the latter. Hence, it is also clear that the value of  $\omega_m$  depends weakly on the actual form of the function  $\rho_v(\epsilon)$  (Refs. 29 and 31).

Figure 8 also shows another characteristic feature of the observed luminescence spectra of heavily doped semiconductors: at low temperatures the energy of the spectral maximum  $\omega_m$  decreases in direct proportion to temperature and the rate of decrease is much greater than that of  $E_g(T)$ . This dependence of  $\omega_m$  on  $T$  can be explained by the fact that increase in temperature results in thermal liberation of carriers from the deeper levels in the valence band tail, so that  $\epsilon_p^0$  shifts into the band. Then the slope of  $\omega_m(T)$ , as indicated by Eqs. (2.11) and (2.6a), is governed by  $\ln[N_v(p + \theta_0 n)^{-1}]$ . Estimates indicate that  $\theta_0 = \bar{W}_n^0/W_p$  amounts to  $10^{-1} - 10^{-3}$ . Moreover, we must bear in mind that, beginning from certain values of  $n_0$ , nonradiative capture of a hole by localized tail states may be controlled by the Auger recombination process<sup>75,95</sup> when  $W_p \propto n_0^{-1}$  and, therefore,  $\theta n_0$  clearly does not exceed  $10^{14} - 10^{16} \text{ cm}^{-3}$ .

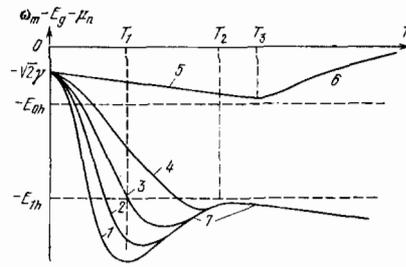


FIG. 9. Qualitative temperature dependences of the energy of the luminescence maximum of a degenerate heavily doped semiconductor with different carrier densities. The initial parts of curves 1–5 correspond to Eq. (2.11), the number of the curve increasing with the carrier density (rate of excitation). Segments 6 and 7 correspond to Eqs. (2.14) and (2.15), respectively.

Thus, in the case of  $n$ -type heavily doped semiconductors we find that  $\ln(N_v/\theta n_0) \approx 5-7$  at low rates of excitation. A slope of approximately this kind is exhibited by a number of heavily doped semiconductors: InAs (Ref. 99; see Fig. 8 in the present paper), GaAs (Refs. 100–102), CdS (Ref. 103), and CuInSe<sub>2</sub> (Ref. 104).

Not only the initial slope, but also the general form of the function  $\omega_m(T)$  depends strongly on the degree of doping and the rate of excitation (pumping). This function has a minimum (Fig. 9) near a temperature equal to  $\min(T_1, T_3)$ , where

$$T_1 = \max \left\{ \left[ \left( \frac{2}{3} \right)^2 \lambda I_a T_0^2 \ln^{-1}(N_v(p + \theta_0 n)^{-1}) \right]^{1/3}, E_{th} \ln^{-1}(N_v(p + \theta_0 n)^{-1}) \right\}, \quad (2.12)$$

$$T_3 = \max \{ (\gamma^2 \gamma_{h,1/2})^{1/3}, \gamma \ln^{-1/2}[N_v(p + n\theta_0)^{-1}] \}. \quad (2.13)$$

In the case of heavy doping and high rates of excitation, when  $p + \theta_0 n$  is large, we have  $T_1 > T_3$ , i.e., the minimum of  $\omega_m(T)$  is located at  $T_{min} = T_3$ , whereas at low electron and hole densities it is located at  $T_{min} = T_1$ . The reason for this behavior of  $\omega_m(T)$  is that at low values of  $p + \theta_0 n$  the value of  $\epsilon_p^0$  becomes greater than  $E_{oh}$  before the condition  $\epsilon_p^0 < \gamma^2/T$  is violated, i.e., the value of  $\epsilon_p^0$  emerges from the Gaussian tail region [Eq. (2.3a)]. In the case of heavy doping and high excitation rates this does not occur, i.e., the maximum of the luminescence spectrum corresponds to the recombination of electrons and holes localized in the Gaussian tail states at all temperatures. In the range  $T > T_3$  the distribution of holes between the Gaussian tail states is essentially quasiequilibrium. Then, it follows from Eqs. (2.6) and (2.3a) that the maximum of the number of filled states in the tail  $\rho_v(\epsilon)q_h(\epsilon)$  corresponds to<sup>105</sup>  $\epsilon = \gamma^2/T$  and this determines the value of  $\omega_m$  (Ref. 29):

$$\omega_m = \mu_n + E_g - \frac{\gamma^2}{T} - T \ln \left( \frac{2\mu_n}{T} \right) \quad (T > T_3). \quad (2.14)$$

It follows from Eq. (2.14) that an increase in temperature shifts  $\omega_m$  toward shorter wavelengths (compare Figs. 9 and 7) and this frequency ceases to depend on the excitation rate. This behavior of  $\omega_m$  is due to the fact that an increase in temperature makes the distribution of nonequilibrium holes between localized tail states increasingly more uniform. Since the number of shallow localized states (with energies close to  $E_v$ ) is much greater than the number of deep states, the former begin to dominate radiative recombination in

heavily doped semiconductors. The value of  $\omega_m$  is independent of the rate of excitation at high temperatures because the probability of occupancy of shallow states is then low.

However, if  $p + \theta_0 n$  is small then, beginning from a certain temperature when  $\epsilon_p^0$  becomes larger than  $E_{0h}$ , luminescence is governed by electron transitions to deep tail states. Such radiative transitions occur only because of the tunneling of carriers (Fig. 6) so that Eq. (2.11) for  $\omega_m$  now contains appropriate corrections,<sup>31</sup> which do not alter the dependence  $\omega_m(T)$  in the range  $T < T_1$  provided  $m_c \ll m_n$ . At temperatures  $T > T_1$ , the thermal spreading of the step describing the occupancy of localized states in the valence band tail, given by Eq. (2.6), has the effect that  $\omega_m$  is governed by fluctuations with  $\epsilon > E_{1h}$  [Eq. (2.3b)] and it is given approximately by<sup>31</sup>

$$\omega_m = \begin{cases} E_g + \mu_n + \frac{4}{3} \pi \sqrt{\frac{m_e \lambda I_a}{m_h \mu_n}} T_0 - \lambda I_a \left( \frac{2T_0}{3T} \right)^2, & T_1 < T < T_2, \\ E_g + \mu_n - E_{1h} - T \ln \left( \frac{2\mu_n}{T} \right), & T > T_2 \approx \frac{2}{3} \sqrt{\frac{I_a}{E_{1h}}} T_0, \end{cases} \quad (2.15)$$

i. e., when temperature is increased this frequency first shifts toward shorter wavelengths and then toward longer wavelengths (curve 7 in Fig. 9). It should be noted that at these temperatures and excitation rates the luminescence spectrum may have a second maximum  $\omega'_m$  whose position is given by Eq. (2.14). It is clear from Eqs. (2.14) and (2.15) that at high temperatures we have  $\omega'_m - \omega_m \approx E_{1h}$  (Fig. 9), which can be used to estimate experimentally the value of  $E_{1h}$  (Ref. 31).

It follows that at all excitation rates the dependence  $\omega_m(T)$  is nonmonotonic and the degree of nonmonotonicity decreases on increase in the rate of excitation (Fig. 9). This evolution of the spectrum follows from Eq. (2.10) and it explains the temperature dependences of  $\omega_m$  observed experimentally for  $n$ -type GaAs at different excitation rates.<sup>100,106,107</sup> It should be noted that the observed dependence  $\omega_m(T)$  is influenced by the temperature dependence of the band gap:  $E_g = E_g^0 - \beta T$ . It is clear from Eq. (2.11) that this has the particular effect that at temperatures  $T > T_4 = \gamma \beta^{-1/2}$  the value of  $\omega_m$  decreases on increase in  $T$ . For GaAs with  $N_d \approx 10^{16} \text{ cm}^{-3}$  we have  $T_4 \approx 150\text{--}200 \text{ K}$ , which is in agreement with the experimental results.<sup>100,106,107</sup>

It is clear from an analysis of Eq. (2.10) that<sup>31</sup> the dependence of the probability of radiative recombination on the carrier energy, given by Eq. (2.8), is manifested—as expected—by the fact that the fall of  $\Phi(\omega)$  at long wavelengths does not repeat the behavior of  $\rho_v(\epsilon)$ . This should be particularly noticeable in the case of sufficiently strongly compensated heavily doped semiconductors when  $\mu_n \approx (m_e/m_h)^{1/3} \gamma_{h,3/2}$ . In the far long-wavelength region the strong dependence of the probability of radiative recombination on the photon energy, given by Eq. (2.8), may give rise to a temperature dependence of the profile of the long-wavelength edge of the luminescence spectrum of strongly compensated heavily doped semiconductors.<sup>31</sup>

At sufficiently high temperatures the process of in-

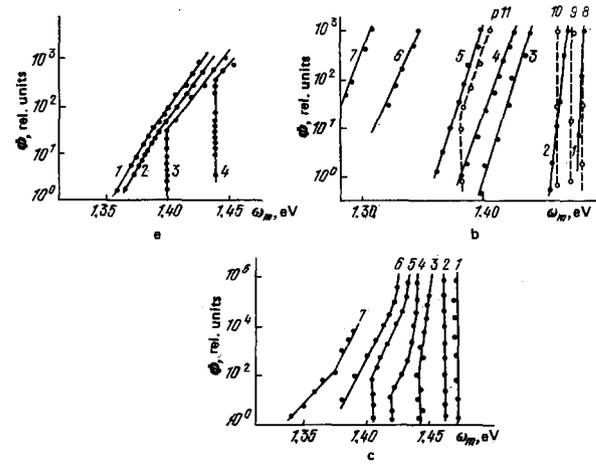


FIG. 10. Dependence of the position of the spectral maximum of the luminescence of compensated GaAs on the intensity of this maximum: a) electroluminescence of a  $p$ - $n$  junction at various temperatures<sup>105</sup> (1—77°K, 2—98°K, 3—188°K, 4—300°K); b) photoluminescence of  $n$ -type samples<sup>112</sup> at  $T = 77^\circ\text{K}$ , numbers of the dependences from 1 to 6 correspond to an increase in the degree of doping from  $N_d = 3.5 \times 10^{17} \text{ cm}^{-3}$  to  $N_d = 7 \times 10^{18} \text{ cm}^{-3}$  and a low degree of compensation  $K = N_d/N_a \approx 3\text{--}10$ , curve 7 represents a strongly compensated  $n$ -type sample,<sup>113</sup> dashed curves 8—10 correspond to a weakly compensated  $p$ -type material<sup>112</sup> (8— $N_a = 8 \times 10^{17} \text{ cm}^{-3}$ , 9— $N_a = 5 \times 10^{18} \text{ cm}^{-3}$ , 10— $N_a = 5 \times 10^{19} \text{ cm}^{-3}$ ), and curve 11 corresponds to a strongly compensated  $p$ -type sample<sup>113</sup>; c) luminescence of  $p$ -type samples<sup>98</sup> at  $T = 77^\circ\text{K}$  due to excitation of carriers from a heterojunction ( $N_a = 1.5 \times 10^{18} \text{ cm}^{-3}$ ), increasing numbers of curves correspond to an increase in the degree of compensation from  $K = 15$  to  $K = 0.94$ .

terband radiative recombination is governed mainly by band-band transitions (BB in Fig. 6). The spectrum of such luminescence can be calculated in the usual way (see Sec. 1 c) using the concept of the quasi-Fermi level of holes.<sup>38,108,109</sup> At intermediate temperatures the luminescence spectrum of a heavily doped semiconductor may have two maxima due to BT and BB transitions, respectively (Fig. 6). Such spectra have been observed in several experiments<sup>99,101</sup> (Fig. 8).

According to the experimental results obtained in investigations of the electroluminescence of heavily doped semiconductors<sup>7,13,18,105-111</sup> at relatively low temperatures, an increase in the rate of injection shifts  $\omega_m$  toward shorter wavelengths. It has been found subsequently<sup>98,112,113</sup> that the magnitude of the shift depends strongly on the type of conduction of a heavily doped semiconductor and on the degree of its compensation (Fig. 10). These results can be explained on the basis of Eq. (2.11). In fact, at nonequilibrium hole densities satisfying  $p > \theta_0 n_0$  the quantity

$$\epsilon_p^0 = T \ln [N_v (p + \theta_0 n)^{-1}]$$

decreases and, consequently,  $\omega_m$  increases on increase in the rate of excitation. As pointed out earlier, we find that  $\theta n_0 \approx 10^{14}\text{--}10^{16} \text{ cm}^{-3}$  and this quantity decreases when the degree of compensation is increased and, therefore, the condition  $p > \theta n_0$  may be obeyed even at low excitation rates. The physical reason for this increase in  $\omega_m$  can easily be established if we bear in mind that  $\epsilon_p^0$  of Eq. (2.6a) is the ionization energy of

that acceptor level in a tail for which the frequency of hole capture and subsequent recombination is equal to the frequency of thermal release of holes. An increase in the hole density results in an increase in the rate of their capture and this reduces the value of  $\varepsilon_{\nu}^0$ , consequently,  $\omega_m$  increases in accordance with Eq. (2.11).

At higher temperatures ( $T > T_1$  or  $T_3$ ), it follows from Eqs. (2.14) and (2.15) that the position of the spectral maximum is independent of the rate of excitation up to very high values of the latter. The higher the temperature, the faster the rate of excitation from which  $\omega_m$  begins to rise on increase in this rate. This conclusion follows from an analysis of Eq. (2.10) and is confirmed by the experimental results (Fig. 10a).

We shall now consider the reason for the difference between the excitation-rate dependences of  $\omega_m$  observed for  $n$ - and  $p$ -type heavily doped semiconductors at low temperatures ( $T = 77^\circ\text{K}$ ) and low rates of excitation (Figs. 10b and 10c). This dependence is governed mainly by the occupancy of the tail states with the minority carriers. The characteristic parameters of the impurity potential are determined by the majority carriers and the energy of localization  $\varepsilon_0 = \hbar^2/m^*r_0^2$  in a typical potential well of size  $r_0$  and of depth  $\gamma$  depends strongly on the carrier mass.<sup>27</sup> A bound state forms in a typical potential well if  $\varepsilon_0 < \gamma$ . In the case of  $n$ -type semiconductors this condition is usually satisfied by a hole because of its large effective mass. For example, in the case of  $n$ -type GaAs, it is obeyed beginning from  $N_d \approx 5 \times 10^{17} \text{ cm}^{-3}$ . Consequently, this material exhibits an extended valence band tail, whose energy size increases on increase in the degree of doping. This accounts for the considerable rise in  $\omega_m$  when the rate of excitation is increased, observed for  $n$ -type GaAs (Fig. 10b), which becomes greater for higher degrees of doping. In the case of  $p$ -type samples the situation is usually opposite. Electrons have a small effective mass and do not form bound states in typical potential wells even when  $N_a \approx 10^{19} \text{ cm}^{-3}$ . For this reason the energy size of the conduction band tail remains very small right up to these high acceptor concentrations.<sup>11</sup> Consequently, even at fairly low temperatures it is found that localized states in the conduction band tail become thermally emptied and the dependence of  $\omega_m$  on the rate of excitation disappears. In other words, the characteristic temperatures  $T_1$ ,  $T_2$ , and  $T_3$  are very low in the case of  $p$ -type GaAs. This accounts for the absence of the dependence of  $\omega_m$  on the rate of excitation in the case of uncompensated  $p$ -type GaAs samples<sup>112</sup> at the same temperatures and for the same degrees of doping as in the case of  $n$ -type samples, which clearly show this dependence (Fig. 10b). Moreover, the same reasons account for the fact that the dependence  $\omega_m(T) - E_g(T)$  observed for  $p$ -type GaAs has, in contrast to  $n$ -type samples, only a rising part at  $T \geq 77^\circ\text{K}$  (Ref. 107). Compensation of  $p$ -type semiconductors results, in the final analysis, in partial

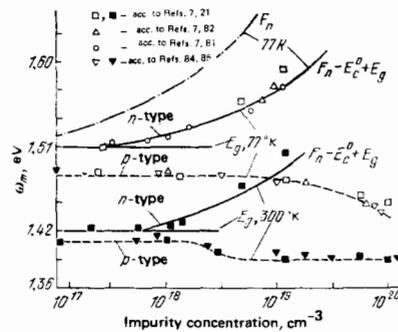


FIG. 11. Summary of the experimental data of Refs. 7, 18, 21, 81, 82, 84, 85 on the dependence of the energy of the spectral maximum  $\omega_m$  on the degree of doping. The open symbols correspond to  $77^\circ\text{K}$  and the dark symbols to  $295^\circ\text{K}$ . The chain curve shows the position of the Fermi level of electrons  $F_n$  at  $77^\circ\text{K}$ , and the continuous curve the value of  $F_n - E_c^0 + E_g$ .

emptying of states in the valence band tail and this begins to manifest itself in the luminescence. For the same reason it is found that, the higher the degree of compensation of  $p$ -type samples, the lower are the rates of excitation at which the dependence of  $\omega_m$  on the pumping rate becomes important (Fig. 10c and Sec. 2 e).

Thus, the position of the spectral maximum depends strongly on temperature, as well on the nature and concentration of the dopant, degree of compensation, and rate of excitation. Therefore, an analysis of the dependence of  $\omega_m$  only on the degree and nature of doping, which has been made in some of the reviews, seems pointless. It is meaningful only in the case of very low or very high temperatures and also in the case of high rates of excitation when, according to Eqs. (2.11) and (2.14), we have  $\omega_m \approx \mu_{n,p} + E_g \approx F_{n,p} - E_{c,v}^0 + E_g$  for degenerate  $n$ - and  $p$ -type semiconductors, respectively. Figure 11 shows the results of various investigations of GaAs which represent, in our opinion, precisely these cases. We can see that an increase in the degree of doping of  $n$ -type samples increases  $\omega_m$  considerably, but decreases it in the case of  $p$ -type samples. The change in  $\omega_m$  on increase in the impurity concentration is governed, on the one hand, by an increase in the Fermi energy  $\mu_{n,p} = F_{n,p} - E_{c,v}^0$  and, on the other, by the concentration-narrowing of  $E_g$  given by Eq. (2.4). In the case of  $n$ -type semiconductors the smallness of  $m_n$  ensures that the first factor predominates, whereas in the case of  $p$ -type semiconductors the second factor is the more important. In fact, the large value of  $m_n$  makes  $p$ -type semiconductors degenerate only for  $N_a \geq 5 \times 10^{19} \text{ cm}^{-3}$ . At lower acceptor concentrations the holes are nondegenerate and, therefore, the energy of the spectral maximum is  $\omega_m \approx E_g - T$  (see Sec. 1 c), i. e., the dependence of this energy on the acceptor concentration is entirely due to the band narrowing of Eq. (2.4).

We recall that the above results apply to injection pumping of photoexcitation with photons of energy  $\Omega > F_n - E_v, E_g$  (see Footnote 5). At lower energies of the exciting photons, for example, when  $\Omega < E_g$ , the absorption of light can only be due to the ionization of

<sup>11</sup> Experimental data<sup>114</sup> on the frequency dependence of the absorption coefficient of heavily doped GaAs also indicate that the density-of-states tail appears for the minority carriers only in  $n$ -type crystals.<sup>27</sup>

levels in the deep tail of the valence band, i. e., localized rather than free holes are generated optically (Fig. 6). The probability of this process is given by Eq. (2.8) where  $E_c = E_h + \Omega$  and the photoionization cross section  $\sigma_{ph}(E_h, \Omega)$  differs significantly from zero at low values of  $T$  only if  $E_h > F_n - \Omega$ . In this case we can calculate  $\Phi(\omega)$  from Eqs. (2.7) and (2.6) but we must replace  $pW_p$  with  $\sigma_{ph}(E_h, \Omega)I$ . It is then clear that the luminescence spectrum has only frequencies  $\omega < \Omega$  right up to high temperatures and  $\omega_m$  is close to  $\Omega$ .

We can thus see that the photoluminescence and injection luminescence spectra may differ significantly both in respect of the form and nature of their temperature dependence. Differences of this kind have been observed experimentally.<sup>107</sup>

### c) Impurity radiative recombination in heavily doped semiconductors

As pointed out earlier, the majority of direct-gap semiconductors is characterized by  $m_c \ll m_h$  and when the impurity concentration is  $10^{17} - 10^{19} \text{ cm}^{-3}$  the heavy doping condition is satisfied for donors ( $N_d a_c^3 > 1$ ) but not for acceptors ( $N_a a_h^3 \ll 1$ ). In other words, the wave functions of even shallow isolated acceptors are strongly localized and we can ignore their overlap at such impurity concentrations, i. e., an impurity band defined in the usual way<sup>89,91</sup> does not form. Nevertheless, fluctuations of the donor concentration result in smearing of the acceptor level. If then  $\gamma < I_a$ , the density of states  $\rho_v(\varepsilon)$  has a maximum at the acceptor ionization energy  $I_a$  (Fig. 6) where this density is<sup>27</sup>

$$\rho_v(E_h) \equiv \rho_a(E_h) = \frac{N_a}{\sqrt{2\pi}\gamma} \exp\left[-\frac{(E_h - E_v^0 - I_a)^2}{2\gamma^2}\right]. \quad (2.16)$$

When this situation occurs in an  $n$ -type semiconductor, its luminescence is governed by the recombination of free electrons of energy  $E_c \approx F_n$  with holes localized at acceptors. In fact, nonequilibrium holes which appear in a sample because of illumination or injection are first captured by the acceptor states and then they recombine. In this case, it is natural to speak of impurity radiative recombination in heavily doped semiconductors, governed by band-impurity transitions (BI channel; Fig. 6).

The potential due to fluctuations of the impurity concentration is fairly smooth if  $N_d r_0^3 \gg 1$  and, therefore, we can adopt the bent band approximation for holes because of their large mass. This means that in investigations of impurity recombination we can regard a heavily doped semiconductor as an array of volume elements of size  $r_0$ , in each of which recombination takes place as described in Sec. 1 d. The position of the top of the valence band in a given elementary volume is governed by the local fluctuation of the potential  $V$  and the Fermi level of degenerate electrons is the same for the whole crystal (Fig. 6). As a result, the energy of a spectral luminescence maximum varies from one elementary volume to another and this determines the position and profile of the luminescence line.<sup>32</sup>

A similar situation may occur also in nondegenerate

compensated heavily doped semiconductors with a small effective electron mass. In fact, if  $\hbar^2/m_c r_0^2 > \gamma$ , bound states do not form in typical potential wells and electrons tunnel easily across potential humps with the same characteristic dimensions. In this case, the conduction band of a heavily doped semiconductor is practically unaffected by fluctuations of the impurity potential, i. e., the position of the bottom of this band is the same throughout a crystal<sup>25,30</sup> (see, however, Sec. 2 d).

In considering the hole capture kinetics we have to distinguish two types of acceptor level.<sup>32</sup> The first type is located in those parts of the crystal where the top of the bent band  $E_v^0 + V$  lies above the percolation level  $E_v$ , i. e., where the impurity potential represents a hump for holes. These levels are responsible for the  $BI_1$  luminescence (Fig. 6). The second type of level is located in those regions where the valence band edge lies above the percolation level. Such acceptor levels are responsible for the  $BI_2$  luminescence channel. The capture of free holes at levels of the second type is a two-stage process. Initially a hole is captured nonradiatively by a localized tail state (see Sec. 2 b) and then by an acceptor level (Fig. 6). The mechanism of hole capture by such an acceptor level is analogous to the cascade mechanism<sup>96</sup> for which the capture probability  $W_p$  depends weakly on the impurity ionization energy. For this reason we are justified<sup>32</sup> in adopting the model of a set of acceptor levels with an ionization energy  $I_a + V - \gamma_h$ , whose occupation probability for regions with  $V \geq \gamma_n$  is given by Eq. (2.6), where  $\theta$  can be regarded as practically constant.

In the case of recombination via levels of the first type an important factor is the thermally activated nature of the capture of holes by these levels. In fact, we can find a hole in a region where the top of the valence band  $E_v^0 + V$  lies below the percolation level  $E_v$  (Fig. 6) only if the hole has the appropriate thermal energy (the hole is regarded as a quasiclassical particle). The probability of filling of these levels is given by Eq. (1.28), where we have to allow for the fact that the density of holes in the regions where  $E_v^0 + V \leq E_v$  is, in accordance with the Boltzmann distribution,  $p(V) = p \exp[(E_v^0 + V - E_v)/T] = p \exp[(V - \gamma_h)/T]$ . Bearing these features of the hole capture in mind, we find that the probability of filling of acceptor levels can be written in the form<sup>32,33</sup>

$$g_a(V) = \frac{N_a^0(V)}{N_a} = p \left[ p + \theta n \eta(V) + N_v \exp\left(\frac{\gamma_h - V - I_a}{T}\right) \right]^{-1}, \quad (2.17)$$

where

$$\theta = \frac{W_n}{W_p}, \quad \eta(V) = \begin{cases} 1 & \text{for } V > \gamma_h, \text{ i. e. } E_h > E_v \equiv E_v^0 + \gamma_h, \\ \exp\left(\frac{V - \gamma_h}{T}\right) & \text{at } V < \gamma_h. \end{cases}$$

If we know the local concentration of neutral acceptors  $N_a^0(V)$ , the spectral intensity of the luminescence emitted by a given point in a crystal can be calculated from a formula analogous to Eq. (1.20):

$$\Phi_{BI}(\omega, V) = \omega N_a^0(V) \int \tilde{W}_n(E_e, V) \frac{\rho_c(E_e) \delta(E_e - E_v^0 - V - I_a - \omega)}{1 + \exp[(E_e - F_n)/T]} dE_e, \quad (2.18)$$

where  $\tilde{W}_n(E_e, V) \equiv W_{e,a}$  is the probability of radiative recombination of a free electron of energy  $E_e$  and a hole

localized at an acceptor. It follows from Eq. (1.4) that this probability is practically independent of the energies of the free electron and the localized hole. In fact, the circumstance that the acceptor level is broadened by an amount of the order of  $\gamma$  does not affect the nature of the wave function of a hole localized at an acceptor because, by hypothesis, we have  $r_0 \gg a_h$ , and the wave function of an electron with  $E_c \approx F_c$  is, as pointed out in Sec. 2a, a Bloch function. This makes it possible to use Eq. (1.21) for  $\rho_c(E_c)$ . Averaging  $\Phi_{BI}(\omega, V)$  over the potential fluctuations, which are Gaussian<sup>27</sup> if  $V \lesssim \gamma$ , we shall determine the spectral intensity of the luminescence<sup>32</sup> due to BI transitions (Fig. 6):

$$\Phi_{BI}(\omega) = \frac{N_a B \omega}{\sqrt{2\pi} \gamma} \int_{-\infty}^{\infty} \frac{\sqrt{\omega - E_g - \gamma_h + V + I_a} \exp\left(-\frac{V^2}{2\gamma^2}\right) g_a(V)}{1 + \exp\left(\frac{\omega - E_h + E_v^0 + V + I_a}{T}\right)} dV. \quad (2.19)$$

We note that in the limit  $\gamma \rightarrow 0$  this formula reduces to Eq. (1.22) obtained without allowance for the broadening of the acceptor levels.

Characteristic features of the impurity luminescence spectra of heavily doped semiconductors can be illustrated conveniently for the case when electrons are non-degenerate, but because of the smallness of  $m_c$  we can ignore distortions of the bottom of the conduction band caused by fluctuations of the impurity concentration (see Sec. 2d). In this case Eq. (2.19) assumes the following form for temperatures  $T < \gamma$ :

$$\Phi_{BI}(\omega) = \Phi_{BI1} + \Phi_{BI2} = \frac{N_a B \omega}{\sqrt{2\pi} \gamma} \frac{n p \exp\left[-\frac{(\omega - \omega_a - \gamma_h + 0.5T)^2}{2\gamma^2}\right]}{p + \theta n \eta(\omega) + N_v \exp\left(\frac{\omega - E_g}{T}\right)}, \quad (2.20)$$

where

$$\eta(\omega) = \begin{cases} 1, & \text{for } \omega \leq \omega_a \equiv E_g - I_a, \\ \exp\left(\frac{\omega - \omega_a}{T}\right), & \text{for } \omega \geq \omega_a. \end{cases}$$

It is clear from Eq. (2.20) that at low temperatures and low rates of excitation the energy of the spectral luminescence maximum is  $\omega_m^{BI} = E_g - I_a$ ; the characteristic scale of the fall of  $\Phi_{BI}(\omega)$  at long wavelengths is the quantity  $\gamma$  whereas at short wavelengths it is  $T$ . At higher temperatures ( $T \gtrsim \gamma_h = E_v - E_v^0$ ; see Fig. 6) or at higher rates of excitation, when

$$p \gg p^* \equiv [0n + N_v \exp(-\frac{I_a}{T})] \exp\left(\frac{\gamma_h}{T}\right), \quad (2.21)$$

the value of  $\omega_m^{BI}$  rises by an amount  $\gamma_h$  and the luminescence line broadens assuming the Gaussian shape. The changes in  $\omega_m^{BI}$  are described approximately by the expression<sup>33</sup>

$$\omega_m^{BI} = E_g - I_a + 0.5T + \gamma_h p / (p + p^*)^{-1}. \quad (2.22)$$

In the case of degenerate  $n$ -type heavily doped semiconductors we find from Eq. (2.19) that

$$\omega_m^{BI} \approx F_h - E_v - I_a - \frac{3}{2} \frac{\gamma^2}{F_h - E_c} + T \ln \frac{2(F_h - E_c)}{T} + \gamma_h \frac{p}{p + p^*}. \quad (2.23)$$

In both cases the behavior of  $\omega_m^{BI}$  is due to the thermally activated nature of the filling of acceptor levels of the first type, located in those regions of a crystal where the top of the valence band is below the percolation level  $E_v$ , i.e., where the impurity potential is a

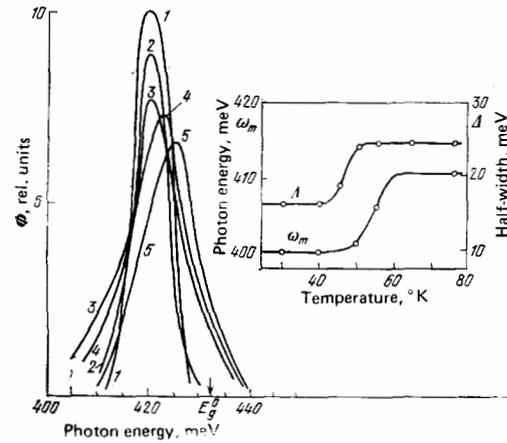


FIG. 12. Impurity luminescence spectra of  $n$ -type InAs samples<sup>116</sup> ( $n = 1.5 \times 10^{16} \text{ cm}^{-3}$ ) at various temperatures  $T$  (°K): 1) 30; 2) 40; 3) 50; 4) 56; 5) 77. The inset shows the temperature dependences of the position of the maximum  $\omega_m$  and of the half-width of the luminescence line  $\Delta$ .

hump for holes (Fig. 6). In fact, since  $E_v$  lies  $\gamma_h$  above the edge of the unperturbed valence band  $E_v^0$ , the maximum of the function  $\rho_a(E_h)$  of Eq. (2.16) is located in the energy range corresponding indeed to acceptor levels of the first type. Increase in temperature or in the rate of excitation results in filling of these levels and this broadens the luminescence line and shifts its maximum toward shorter wavelengths by  $\gamma_h$ . These effects are observed, for example, in GaAs doped with Mn (Ref. 115) and in moderately doped  $n$ -type InAs (Refs. 116 and 117; see Fig. 12 in the present paper).

It should be stressed that, as in Sec. 2b, the distribution of holes between the acceptor states (2.17) differs considerably from the quasiequilibrium form. This is not surprising because the results given here differ qualitatively from the conclusions obtained on the assumption of a quasiequilibrium distribution of holes. If the latter were true,<sup>12)</sup> the long-wavelength edge of the luminescence line would have become saturated and  $\omega_m^{BI}$  would have been governed by the difference of the corresponding quasi-Fermi levels, i.e., it would have depended strongly on the rate of excitation.<sup>118,119</sup> On the other hand, if the true nature of the hole distribution (2.17) is allowed for, it is found that, in accordance with Eqs. (2.19) and (2.20), the intensity  $\Phi_{BI}(\omega)$  increases proportionally to the nonequilibrium hole density if  $p < \theta n$  and  $\omega < E_c - I_a$ , and this is in agreement with the experimental results.<sup>18,120</sup> In fact, this follows even from the theory of Shockley-Read impurity recombination<sup>54</sup> and is reflected in Eq. (1.22), describing the luminescence spectrum without allowance for the broadening of the acceptor level. We can see from Eqs. (2.22) and (2.23) that the value of  $\omega_m^{BI}$  depends

<sup>12)</sup> The distribution of holes between the acceptor states may be of quasiequilibrium type even at low temperatures, when these states overlap strongly, i.e., when a wide impurity band with a high carrier mobility is formed. In this case holes may have time to be redistributed between the states in such an impurity band by hopping conduction<sup>89,91,28</sup> before they recombine with electrons.

weakly on the rate of excitation and changes only by an amount  $\gamma_h$  in a narrow range of temperatures and excitation rates (Fig. 12).

#### d) Interimpurity radiative recombination in heavily doped semiconductors

If under the doping conditions considered in the preceding subsection we have  $N_a > N_d$ , the luminescence of such a *p*-type semiconductor observed at moderately high temperatures and excitation rates is governed by the recombination of nonequilibrium electrons with holes localized at acceptors. Transitions of the BI and TI type (Fig. 13) determine the luminescence spectrum at lower frequencies than those corresponding to interband recombination channels (TT, BT, BB). Since the luminescence spectrum due to BI transitions is considered in the preceding subsection, we shall concentrate here on the radiative recombination corresponding to the TI channel (Fig. 13). Transitions of the TI type represent the recombination of electrons captured by localized states in the conduction band tail and holes localized in one of the neighboring acceptors. Such interimpurity recombination represents the same mechanism into which the donor-acceptor recombination transforms (see Sec. 1 e) in compensated heavily doped semiconductors.<sup>33</sup>

As in Sec. 2 c, we shall assume that (because of the smallness of  $m_c$ ) an electron does not form a bound state not only at a single donor, but also in a typical potential well of depth  $\gamma$  and size  $r_0$ . Therefore, localized states in the conduction band tail located below the percolation level  $E_c$  (Fig. 13) are governed by the local clusters with sufficiently large numbers of donors, which can be regarded as "point" Coulomb centers with different charges.<sup>27</sup> The density of such states  $\rho_c(E_c)$

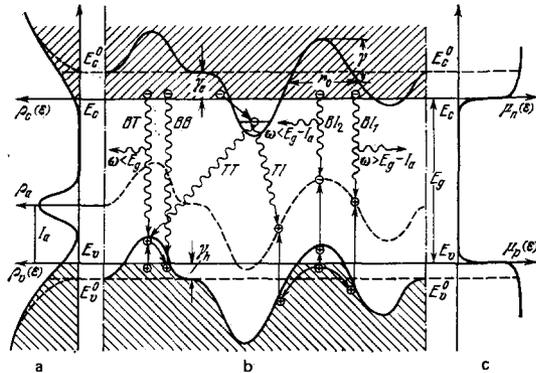


FIG. 13. Energy band diagram and recombination channels of a strongly compensated (nondegenerate) heavily doped semiconductor: a) density of states; b) energy band diagram; c) dependence of the electron  $\mu_n$  and hole  $\mu_p$  mobilities on their energy. Here,  $E_c$  and  $E_v$  are the percolation levels of electrons and holes, respectively;  $E_c^0$  and  $E_v^0$  are the edges of band gap of an undoped semiconductor;  $I_a$  is the ionization energy of an acceptor level. The wavy lines represent the following recombination channels: tail-impurity (TI) recombination of an electron captured by a localized state in the conduction band with a hole at one of the neighboring acceptors; band-impurity (BI) recombination of a free electron with a hole captured by an acceptor; tail-tail (TT) transitions; band-tail (BT) transitions; band-band (BB) transitions.

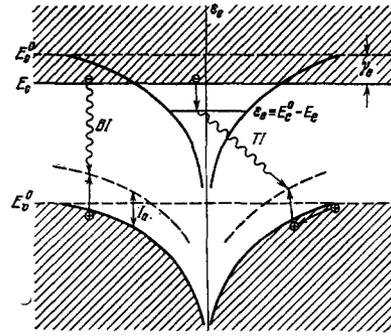


FIG. 14. Energy band diagram near a point-like cluster of donors corresponding to a localized electron state of energy  $E_e$  in the conduction band tail. The shaded regions represent the continuous carrier spectrum. The wavy lines identify radiative transitions (Fig. 13).

$-E_c$ ) is given approximately by Eq. (2.3b) with  $\gamma_{c,1/2} \equiv \gamma_0$  and the wave function of a localized electron is hydrogen-like<sup>27</sup> with a Bohr radius  $a_{ez} = a_g z^{-1}$ , where the number of donors in a cluster is  $z = (E_c^0 - E_e)^{-1/2} I_d^{-1/2}$ .

Holes characterized by a large mass can be regarded as quasiclassical particles and their behavior can be described in the bent band approximation. Then, if  $a_h < r_0$ , an acceptor level follows the changes in the edge of the distorted valence band, i.e., its position is governed by the magnitude of local fluctuations of the impurity potential. Consequently, the position of the acceptor level near a potential well created by a local cluster of  $z$  donors depends on the distance  $r$  from the center of the well approximately as (Fig. 14)

$$E_h(r) = E_v^0 + I_a - \frac{e^2 z (E_e)}{\epsilon r}. \quad (2.24)$$

A local density of free holes  $p(r, z)$  near such a well is also a function of the distance from the center of the well. In this case, free holes are not degenerate and their distribution can be described by introducing a quasi-Fermi level  $F_p$ , i.e.,

$$p(r, z) = N_v \exp\left(\frac{E_v^0 - F_p}{T} + \frac{e^2 z (E_e)}{\epsilon r T}\right) \equiv p \exp\left(-\frac{\gamma_h}{T} - \frac{e^2 z (E_e)}{\epsilon r T}\right). \quad (2.25)$$

The probability of the recombination of an electron localized at a cluster with  $z$  donors and a hole captured by an acceptor located at a distance  $r$  from the cluster (Fig. 14) can be written, as in the theory of donor-acceptor recombination (see Sec. 1 e) in the form of Eq. (1.5):

$$v(r, z) = v_0 \exp\left(-\frac{2rz}{a_e}\right). \quad (2.26)$$

The energy of the emitted photons is then given by Eq. (1.31), i.e.,

$$\omega = E_e - E_h + \frac{e^2}{\epsilon r}. \quad (2.27)$$

The number of localized states in the conduction band tail of a heavily doped semiconductor is much less than  $N_d$  so that if  $N_a > N_d$ , near each donor cluster there is a sufficient number of acceptors (Fig. 14). This makes it possible to study the recombination of localized carriers by considering only the processes occurring near one cluster. The probability of occupation of an acceptor  $i$  near a well of depth  $\epsilon_e = (E_c^0 - E_e)$  is then

given by<sup>33</sup>

$$\frac{\partial q_h}{\partial t} = p(r_1, E_e) W_p (1 - q_h) - W_p N_v e^{-I_a/T} q_h - n W_c q_h - v(r_1, E_e) q_h q_e, \quad (2.28)$$

where  $\bar{W}_p$  is the probability of the capture of a hole by an acceptor and  $\bar{W}_n$  is the probability of recombination of a free electron with a hole localized at an acceptor. In this case the value of  $W_p$  or  $\bar{W}_n$  depends weakly on the carrier energy (see, however, Sec. 2e). The distribution of electrons from localized tail states is of the quasiequilibrium type,<sup>33</sup> i.e.,

$$q_e \equiv f(E_e) = \left[ 1 + \exp\left(\frac{E_e - F_n}{T}\right) \right]^{-1}, \quad (2.29)$$

where  $F_n = E_c - T \ln(N_c/n) \equiv E_c - \mu_n$  is the quasi-Fermi level of electrons. This is due to the fact that at low temperatures a hole cannot approach sufficiently closely a donor well (Fig. 14) and become captured by the acceptor nearest to this well. Therefore, a localized electron may recombine only with holes located at distant acceptors and the probability of such a process given by Eq. (2.26) is low. Consequently, thermal release of electrons from walls predominates over the loss by recombination even at low temperatures and this results in electron thermalization. The distribution of holes between acceptors differs considerably from the quasiequilibrium form because of high ionization energy of acceptors  $I_a$  allows us to ignore the thermal release of holes. The probability that a hole occupies an acceptor under steady-state conditions follows from Eqs. (2.28) and (2.29):

$$q_h = \frac{p(r_1, E_e) W_p}{p(r_1, E_e) W_p + W_p N_v \exp(-I_a/T) + n \bar{W}_n + v(r_1, E_e) f_e(E_e)} \quad (2.30)$$

and it is governed mainly by the rates of hole capture and recombination.

If we assume that the distribution of acceptors near each donor well is random (see Sec. 1e), the spectral intensity of the luminescence due to TI transitions (Fig. 14) can be represented, by analogy with Eq. (1.32), as follows:

$$\Phi_{TI}(\omega) = 4\pi N_a \omega \int_{-\infty}^{\min(E_c, E_g^0 + I_a + \omega)} \rho_c(E_e) v(r, E_e) f_e(E_e) q_h(r, E_e) \frac{dr}{d\omega} r^2 dE_e, \quad (2.31)$$

where  $r$  is expressed in terms of  $E_e$  and  $\omega$  by means of Eqs. (2.24) and (2.27).

A maximum of  $\Phi_{TI}(\omega)$  lies near the energy  $E_e - I_a$  (Fig. 13), where the competing mechanism is the impurity recombination (see Sec. 2c). A numerical analysis of Eqs. (2.20) and (2.31) shows<sup>33</sup> that, depending on temperature and rate of excitation, the recombination radiation spectrum at energies  $E_g - I_a$  has one, two, or even three maxima and two of them are related to the TI channel, whereas one is related to the BI channel. An analysis of Eq. (2.31) shows that the temperature dependence of the principal spectral maximum of the TI channel  $\omega_m^{TI}$  depends strongly on the rate of excitation. We shall now explain this result. Radiation of energy  $\omega \approx \omega_m^{TI}$  is due to electron transitions from levels  $E_c \approx F_n$  corresponding to clusters with  $z = z_m = (E_c^0 - F_n)^{1/2} I_d^{-1/2}$ . The value of  $r$  corresponding to the maximum of  $\Phi_{TI}(\omega)$  is determined by the competi-

tion between two factors. The closer the position of an acceptor to the center of a cluster (Fig. 14), the higher is the probability of diagonal radiative transitions given by Eq. (2.26), but the lower the probability of occupation of an acceptor by a hole given by Eq. (2.30). It follows from Eq. (2.31) and from Eqs. (2.3b), (2.25), (2.26), and (2.30) that

$$\Phi_{TI}(\omega) \sim v(r) q_h(r, z) \rho_c(F_n) \sim v(r) p(r, z) \rho_c(F_n) \sim \exp\left(-\frac{2rz}{a_e} - \frac{e^2 z}{\epsilon r T} - \sqrt{\frac{E_c^0 - F_n}{\gamma_0}}\right), \quad (2.32)$$

and this intensity reaches a maximum at  $r = r_m = a_e I_d^{-1/2} T^{-1/2}$ . The energy of a hole localized at an acceptor located at a distance  $r$  from a donor cluster is  $E_h = E_v^0 + I_a - e^2 z_m / \epsilon r_m$ . Bearing in mind that  $z_m \gg 1$ , we find from Eq. (2.27) that

$$\omega_m^{TI} = E_g^0 - \gamma_e - I_a - T \ln \frac{N_c}{n} + 2 \sqrt{T^2 \ln \frac{N_c}{n} + T \gamma_e}. \quad (2.33)$$

It is clear from Eq. (2.33) that at very low temperatures  $T < \gamma_e \ln^2(N_c/n)$ , we have

$$\omega_m^{TI} = E_g^0 - \gamma_e - I_a + 2 \sqrt{T \gamma_e}, \quad (2.34)$$

i.e., this frequency increases on increase in temperature irrespective of the rate of excitation (value of  $n$ ). When temperature is increased further, the nature of the dependence  $\omega_m^{TI}(T)$  depends strongly on  $n$ . When the excitation is weak ( $n \lesssim 10^{-2} N_c$ ), then  $\omega_m^{TI}$  decreases practically linearly on increase in  $T$  beginning from the lowest temperatures and this is due to the lowering of the electron quasi-Fermi level, i.e., due to thermal liberation of electrons from the shallower donor wells. It should be noted that the energy of the maximum in the luminescence spectrum resulting from interimpurity (donor-acceptor) recombination in lightly doped semiconductors increases when  $T$  is increased (see Sec. 1d), i.e., it is qualitatively different from the dependence  $\omega_m^{TI}(T)$  for heavily doped semiconductors excited at low rates. This change in the nature of the temperature dependence of the spectral maximum of the interimpurity luminescence has been observed, for example, for compensated *p*-type Ge as the degree of its doping is increased.<sup>121</sup>

In the case of strong excitation the majority of donor wells is filled with electrons and, therefore,  $\omega_m^{TI}$  is governed by the Coulomb interaction of a free hole with the shallowest wells. When  $T$  is increased, holes approach these wells more closely, i.e.,  $r_m$  decreases and  $\omega_m^{TI}$  becomes a monotonically rising function of temperature.

It is clear from this discussion why the value of  $\omega_m^{TI}$  (in agreement with numerical calculations<sup>33</sup>) is practically independent of the hole density and this density governs only the luminescence intensity in accordance with Eqs. (2.30) and (2.31). It should be stressed that the actual form of the density of states in the conduction band tail  $\rho_c(E_e)$  also has a weak effect on the nature of the dependences of  $\omega_m^{TI}$  on  $T$  and  $n$ . The form of  $\rho_c(E_e)$  affects the long-wavelength edge of the luminescence spectrum; the fall in the short-wavelength edge region is characterized by  $T$ .

Substituting the value of  $r$  in Eq. (2.32), we find that

$$\Phi_{\text{TI}}(\omega) \propto \exp \left[ - \left( T \ln \frac{N_c}{n} + \gamma_e \right)^{1/2} (4T^{-1/2} + \gamma_0^{-1/2}) \right]. \quad (2.35)$$

Hence, it is clear that the intensity of the interimpurity radiative recombination is low both at low and high temperatures and that it reaches its maximum at a temperature approximately given by

$$T_1 = 2^{4/3} \gamma_e^{2/3} \gamma_0^{1/3} \ln^{-2/3} \frac{N_c}{n}. \quad (2.36)$$

Low-temperature quenching of the TI channel is due to the fact that in the limit  $T \rightarrow 0$  the probability of interimpurity recombination  $\nu(\gamma)$  is low, because holes cannot approach close to donor clusters (Fig. 14). High-temperature quenching is due to lowering of the quasi-Fermi level  $F_n$ , i. e., it is due to the thermal emptying of the increasingly deeper donor wells and also due to the release of holes from acceptors to a band.

When temperature is increased, the interimpurity luminescence spectrum may exhibit quenching as well as a second maximum.<sup>33</sup> The second maximum is due to the fact that an increase in temperature equalizes more and more the occupancies of the donor wells of different depth, i. e., the Fermi step of Eq. (2.29) is flattened. Consequently, there is an increase in the role of radiative recombination of electrons localized in shallower wells whose number is greater than that of deep wells and which can be approached more closely by holes. Since the electron energy in such wells is close to the percolation level  $E_c$ , the position of the second maximum and its temperature dependence are described approximately by Eq. (2.34). Hence, it follows that, in particular, these two maxima are separated by about  $T \ln(N_c/n)$  and, therefore, at high rates of excitation they are indistinguishable.<sup>33</sup>

It thus follows that the interimpurity radiative recombination is significant at low rates of excitation ( $n \ll N_c$ ) at temperatures close to  $T_1$ , given by Eq. (2.36). In the opposite case the impurity recombination mechanism of Eq. (2.20) predominates. The latter mechanism (BI channel) is responsible for the third maximum of  $\omega_m^{\text{BI}}$  in the impurity luminescence spectrum and this maximum shifts toward shorter wavelengths when temperature is increased. The dependence  $\omega_m^{\text{BI}}(T)$  is given by Eq. (2.22) and is discussed in Sec. 2c. In contrast to  $\omega_m^{\text{TI}}$  of Eq. (2.33), the thermal shift of  $\omega_m^{\text{BI}}$  of Eq. (2.22) depends not on the electron density but on the ratio of  $n$  to  $p$  ( $n \propto p$ —Ref. 33), which is governed by the dominant recombination channel.

#### e) Edge luminescence of strongly compensated heavily doped semiconductors

An increase in the degree of compensation  $K = N_a/N_d$  reduces the density of free electrons in an  $n$ -type heavily doped semiconductor and the Fermi level  $F_n$  eventually appears below the percolation level ( $F_n < E_c$ , see Fig. 13). In such a strongly compensated heavily doped semiconductor the mechanism of low-temperature luminescence at low rates of excitation is radiative recombination of localized electrons and holes (TT transitions; see Fig. 13). On reduction in the carrier density the screening radius  $r_0$ , and consequently  $\gamma$  of Eq. (2.2), increase and their values begin to de-

pend strongly on the correlation in the distribution of impurities. For a random distribution of impurities the radius  $r_0$  is particularly large and its order of magnitude is<sup>122</sup>

$$r_0 \approx N_d^{1/3} \bar{n}^{-2/3} \quad (N_d > N_a), \quad (2.37)$$

i. e., it is governed by the total carrier density  $\bar{n}$ , which in equilibrium is equal to  $N_d - N_a$ . In the case of a correlated distribution of impurities the values of  $r_0$  and  $\gamma$  are not so large and they are independent of the degree of compensation and the rate of excitation. The correlation in the distribution of impurities may, in particular, be due to their Coulomb interaction,<sup>25,30,123</sup> which at temperatures exceeding  $T_0$  (diffusion "freezing" temperature<sup>25</sup>) results in a redistribution of impurities. If the intrinsic carrier density at  $T = T_0$  does not exceed the impurity concentration, we can ignore the carrier screening and then<sup>30,123</sup>

$$r_0 = \sqrt{\frac{\epsilon T_0}{4\pi N_d e^2}} \quad (N = N_a + N_d). \quad (2.38)$$

This situation occurs in strongly compensated wide-gap materials, in particular—as indicated by theoretical estimates and experimental investigations<sup>124</sup>—in GaAs with  $N \geq 10^{18} \text{ cm}^{-3}$ . On the other hand, in the case of strongly compensated Ge, there is no correlation in the distribution of impurities.<sup>125</sup> The large value of  $\gamma$ , described by Eq. (2.2), in the case of a strongly compensated heavily doped semiconductor is responsible for the Gaussian form (2.3a) of  $\rho_v(\epsilon)$  in a fairly wide range of energies.

It should be stressed that in the region of the Gaussian tail (2.3a) the fluctuations dominating the density of states [optimal fluctuations of  $\rho_v(\epsilon)$ ] are at large values of  $r_0$  nonoptimal for the optical absorption coefficient<sup>27,126,127</sup> and luminescence intensity.<sup>34</sup> Consequently, there are differences between the dependences  $\rho(\epsilon)$ ,  $\alpha(\omega)$ , and  $\Phi(\omega)$ .<sup>131</sup> In fact, the density of states is governed by wells with the most probable size  $r_0$  (Refs. 27 and 28). The absorption of light of frequencies  $\omega < E_c$  occurs only as a result of diagonal transitions associated with the tunnelling of carriers (TT transitions, see Fig. 13). The probability  $\nu$  of this process decreases exponentially on increase in the size of fluctuations  $R$  and, therefore, the fluctuations governing the form of  $\alpha(\omega)$  have the characteristic size  $\bar{R} < r_0$  (Refs. 27 and 126). The luminescence intensity  $\Phi(\omega)$  is governed, like the probability  $\nu$  of radiative diagonal transitions, by the electron and hole populations of the initial and final states, respectively. Since these populations decrease on increase in the probability of radiative recombination  $\nu$ , it is clear that fluctuations optimal from the point of view of  $\Phi(\omega)$  are of size between  $\bar{R}$  and  $r_0$  and depend on the rate of excitation.<sup>34</sup>

It is clear that the spectral intensity of the recombination radiation generated in a strongly compensated heavily doped semiconductor depends exponentially on  $\omega$ . The argument of the exponential function in  $\Phi(\omega)$  can be found,<sup>34</sup> apart from a factor of the order of unity,

<sup>131</sup> These differences are slight for small values of  $r_0$  and  $m_e$  (see the discussion which follows and also Ref. 29).

by a method similar to the approximation of a uniformly charged sphere.<sup>27</sup> The value of this factor can be found using a more rigorous method of optimal fluctuations.<sup>12a, 12b</sup> This approach gives

$$\Phi(\omega) \sim \int dE_e dE_h \delta(E_e - E_h - \omega) q_e q_h \nu(E_e, E_h, R) P(E_e, E_h, R), \quad (2.39)$$

where  $\langle \dots \rangle$  denotes averaging over the various configurations of the potential. Luminescence of frequency  $\omega = E_e - E_h$  results from the tunneling of carriers across a barrier of height  $\Delta = E_g - \omega$ . In this approximation it is assumed that various barriers of a given height  $\Delta$  differ only in respect of the size  $R$ . The excess number of impurities  $z$  necessary to create a barrier of height  $\Delta$  and size  $R$  is approximately  $\propto R\Delta/e^2$  and, therefore, the probability of the appearance of such a barrier when  $R < r_0$  can be written in the form<sup>27</sup>

$$P(E_e, E_h, R) = P_0 \exp\left(-\zeta \frac{z^2}{NR^3}\right) = P_0 \exp\left(-\zeta \frac{E_g^2 \Delta^2}{e^4 NR}\right). \quad (2.40)$$

If we assume that the energy of a localized hole is close to the bottom of a potential well, the probability of recombination involving tunneling of an electron across such a potential barrier is

$$\nu(E_e, E_h, R) = \nu_0 \exp\left(-\eta \frac{R \sqrt{m_e \Delta}}{\hbar}\right). \quad (2.41)$$

In Eqs. (2.40) and (2.41) the quantities  $\zeta$  and  $\eta$  are coefficients of the order of unity.<sup>27</sup>

We shall now consider the electron  $q_e$  and hole  $q_h$  distribution functions. If  $m_e \ll m_h$ , the electron distribution can be described by introducing a quasi-Fermi level  $F_n$ , whereas the distribution of holes between localized tail states can differ considerably from the quasiequilibrium form.<sup>34</sup> In fact, in view of the smallness of  $m_e$ , we can expect electrons to tunnel readily and the potential wells with identical parameters to have levels shallower than those occupied by holes. Since the majority of electron and hole wells is separated by distances of the order of  $r_0$ , the probability of radiative recombination is negligible for most electrons and holes. Therefore, an electron localized at a level shallower than that of a hole is more likely to be released to a band than to recombine with a hole. This process continues until an electron finds itself at a sufficiently close distance from a localized hole. In other words, the thermal redistribution of electrons is a faster process than the recombination. On the other hand, holes are localized at deeper levels and the probability of their recombination may exceed the probability of their thermal release. The situation largely resembles that encountered in the donor-acceptor recombination process in a lightly doped but strongly compensated semiconductor<sup>32</sup> (see Sec. 1 e).

The probability of radiative recombination decreases exponentially on increase in the distance between an electron and a hole and, therefore, we can calculate  $\Phi(\omega)$  by considering only the nearest electron and hole wells. This approximation is equivalent to allowance for only the nearest donor-acceptor pairs in the theory of interimpurity radiative recombination (see Secs. 1 e and 2 d). In this case the probability of occupancy of a hole well of depth  $E_h$  in the configuration of a potential with a characteristic size  $R$  is given by<sup>34</sup>

$$q_h = pW_p \left[ pW_p + N_v W_p \exp\left(\frac{E_v - E_h}{T}\right) + \nu(\Delta, R) f_e(E_e) \right]^{-1}. \quad (2.42)$$

It should be noted that when carriers are excited optically with light of photon energy  $\Omega > E_g$ , the quantity  $pW_p$  in Eq. (2.42) should be replaced with  $pW_p + \sigma_{ph} I_{ph}$ . If  $\Omega < E_g$ , the situation becomes much more complex but the conclusions reached at the end of Sec. 2 b are still valid.

If we calculate the integral in Eq. (2.39) by replacing the Fermi function  $q_e = q_c$  with a step, we find that<sup>34</sup>

$$\Phi(\omega) \sim \left\langle \frac{pW_p \nu(R, \Delta) P(R, \Delta)}{pW_p + N_v W_p \exp[(E_g^0 - F_n - \Delta)/T] + \nu(R, \Delta)} \right\rangle. \quad (2.43)$$

The function averaged in Eq. (2.43) has a sharp maximum in its dependence on  $R$  so that its average value can be replaced with the most probable value. A similar method has been used to determine the spectral dependence of the absorption coefficient of a strongly compensated heavily doped semiconductor which has the following form<sup>27, 12b</sup> when  $F_n - E_v^0 - \gamma > \omega > \omega_1 = E_g^0 - I_d(\gamma_0/a_c)^{4/3}(Na_c^3)^{2/3}$ :

$$\alpha(\omega) \sim \langle \nu(\Delta, R) P(\Delta, R) \rangle \sim \exp\left[-\beta \left(\frac{\Delta}{I_d (Na_c^3)^{2/3}}\right)^{5/4}\right], \quad (2.44)$$

and in this case the size of an optimal fluctuation is  $\bar{R} \approx a_c (\Delta/I_d)^{3/4} (Na_c^3)^{-1/2}$ . A more rigorous approach<sup>12b</sup> based on the optimal fluctuation method<sup>12a</sup> makes it possible to determine the coefficient  $\beta = 2/5\sqrt{\pi}$  and it shows<sup>127</sup> that the ionization energy of a shallow donor  $I_d$  and its Bohr radius  $a_c$  in Eq. (2.44) should be replaced by the corresponding parameters of an exciton.

It follows from Eq. (2.43) that  $\Phi(\omega)$  has a maximum at  $\omega = \omega_m^{TT}$ , where

$$\omega_m^{TT} = E_g - T \ln \frac{N_c}{n} - T \ln \frac{N_v W_p}{pW_p + \nu(R_m, E_g^0 - \omega_m)}. \quad (2.45)$$

At short wavelengths ( $\omega > \omega_m$ ), we find that<sup>34</sup>

$$\Phi(\omega) \sim \exp\left[\frac{E_g^0 - \omega}{T} - \beta \left(\frac{E_g^0 - \omega}{I_d (Na_c^3)^{2/3}}\right)^{5/4}\right], \quad (2.46)$$

i. e., when  $\omega > \omega_m$ , the fall of  $\Phi(\omega)$  is governed by the value of  $T$ . The shape of the long-wavelength edge of the luminescence spectrum depends strongly on the rate of excitation. A comparison of Eqs. (2.43) and (2.44) shows that at high rates of excitation we have  $\Phi(\omega) \sim \alpha(\omega)$  because  $q_h \approx 1$ . At very low excitation rates we have  $q_h \approx pW_p/\nu(R, \Delta) \ll 1$  and under the  $\langle \dots \rangle$  sign in Eq. (2.43) we are left with the function  $P(R, \Delta)$ . This function has a maximum at  $R_m = r_0$  and  $\langle P(R, \Delta) \rangle$  governs the density of states (2.3a) (see Refs. 27 and 28), so that  $\Phi(\omega)$  can be written in the form

$$\Phi(\omega) \sim \exp\left[-\frac{(E_g^0 - \omega)^2}{2\gamma^2}\right]. \quad (2.47)$$

At intermediate excitation rates the function under the sign  $\langle \dots \rangle$  in Eq. (2.43) has a maximum at  $R = R_m$  [ $R < R_m = a_c \sqrt{I_d}/\Delta \ln(\nu_0/pW_p) < r_0$ ] and then  $\Phi(\omega)$  is described by<sup>34</sup>

$$\Phi(\omega) \sim \exp\left[-\left(\frac{E_g^0 - \omega}{I_d}\right)^{5/2} \frac{\xi}{Na_c^3 \ln(\nu_0/pW_p)}\right], \quad (2.48)$$

where  $\xi$  is of the order of unity. We thus find that only at high rates of excitation when the deep states in the valence band tail are occupied does the fall of  $\Phi(\omega)$  at long wavelengths reproduce the behavior of the absorption coefficient  $\alpha(\omega)$  given by Eq. (2.44). It

follows from a comparison of Eqs. (2.47) and (2.48) with Eq. (2.44) that in other cases the value of  $\Phi(\omega)$  in the range  $\omega < \omega_{m1}$  decreases with reduction in the frequency faster than does  $\alpha(\omega)$ . This feature is evidence of the absence of quasiequilibrium in the distribution of nonequilibrium carriers and it has been discovered in an analysis of the experimental data on the photoluminescence and electroluminescence of compensated GaAs (Refs. 13 and 90). The tunnel nature of the radiative recombination process resulting, in particular, in the absence of a quasiequilibrium in the distribution of localized holes has to be taken into account also in an analysis of the photoconductivity of strongly compensated heavily doped semiconductors. The tunneling makes the size of fluctuations governing the recombination rate considerably less than  $\tau_0$ . This is due to the fact that, although the probability (2.40) of formation of fluctuations of the potential of size  $R < \tau_0$  is low, the probability of radiative transitions (2.41) is high in the case of fluctuations of smaller size. For this reason the recombination process is not thermally activated even in the case of strongly compensated and heavily doped semiconductors characterized by large values of  $\tau_0$ . Thus, the assumption of a thermally activated dependence of the carrier lifetime and a quasiequilibrium distribution of carriers underlying the investigation reported in Refs. 130 and 131 is unjustified in the case of strongly compensated heavily doped semiconductors and it cannot be used in the calculation of the dependence of the photocarrier density on the intensity of illumination. When illumination ceases, the carriers separated by short distances, which determine the rate of recombination, recombine rapidly but this does not alter greatly the total photocarrier density.<sup>14)</sup> In fact, the majority of electrons and holes is separated by high barriers with a characteristic size  $\tau_0$  and, therefore, their recombination time is extremely large. This accounts for the "frozen" photoconductivity effect observed in strongly compensated heavily doped semiconductors.<sup>132</sup>

It should be noted that at high rates of excitation when Eq. (2.48) is valid, the characteristic energy of the fall of  $\Phi(\omega)$  depends on the density of nonequilibrium mobile holes, i. e., in the final analysis it depends on the temperature and rate of excitation. This dependence may be manifested also at lower rates of excitation corresponding to Eq. (2.47). This applies to semiconductors with moderately wide gaps in which the distribution of impurities can be (as pointed out earlier) random and the value of  $\gamma$  depends on the rate of excitation (see the beginning of Sec. 2 e).

It follows formally from Eq. (2.46) that  $\Phi(\omega)$  has a maximum at

$$\omega_{m2}^{\text{TT}} = E_g^0 - (Na_2^0)^2 I_0^2 \left( \frac{2\sqrt{\pi}}{T} \right)^4. \quad (2.49)$$

Since Eq. (2.46) is derived for energies  $\omega > \omega_{m1}$ , the value of  $\omega_{m2}$  determines the spectral maximum only at large values of  $T$  when  $\omega_{m2} > \omega_{m1}$ . Since we have con-

<sup>14)</sup> A similar situation occurs also in strongly compensated semiconductors exhibiting donor-acceptor recombination<sup>73</sup> (see Sec. 1e.)

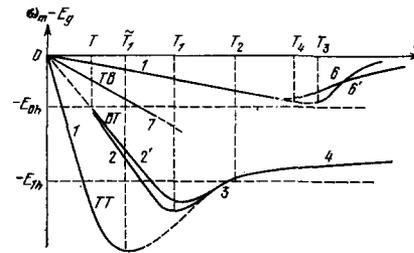


FIG. 15. Qualitative temperature dependences of the energy of spectral maximum of the luminescence emitted by a strongly compensated heavily doped semiconductor. Segments 1-6 of the curves are described by the following formulas: 1) Eq. (2.45), with upper curve corresponding to a higher rate of excitation; 2) Eq. (2.51); 3) Eq. (2.52); 4) Eq. (2.53); 6) Eq. (2.54); 6') Eq. (2.49). Curves labeled 2' and 6' apply to the case of an uncorrelated distribution of impurities.

sidered above the process of radiative recombination only via the Gaussian tail states of Eq. (2.3a), the formulas (2.45) and (2.48) are valid only at  $T < \bar{T}$  (Ref. 31) and  $T > T_3$  (Fig. 15), respectively, when  $E_g^0 - \omega_m < (E_{0h})$ . Hence, it follows that the temperature dependence of  $\omega_m$  is nonmonotonic, as in the case of weakly compensated heavily doped semiconductors (see Sec. 2 b) and this is in agreement with the experimental results.<sup>113,125</sup>

In the intermediate range of temperatures the recombination radiation is governed by carriers localized in deep-tail states associated with point-like acceptor or donor clusters for which the densities of states are given by Eqs. (2.3b) and (2.3c), respectively. In considering the spectrum of such luminescence we have to distinguish<sup>31</sup> the recombination of localized carriers (TT transitions; see Fig. 13) and of free carriers with localized ones (BT and TB transitions; see Fig. 13). Clearly, the spectral maximum corresponding to TT transitions lies at lower photon energies than that corresponding to BT transitions (Fig. 15). Therefore, although at the temperatures under consideration the luminescence is associated mainly with BT transitions,<sup>31</sup> we can expect TT transitions to give rise to an additional long-wavelength maximum whose energy measured at low temperatures ( $T < \bar{T}_1$ ; see Fig. 15) is in fact given by Eq. (2.45) (Ref. 31).

The luminescence spectrum due to BT transitions is described by formulas similar to Eqs. (2.9) and (2.10) but these formulas now apply to nondegenerate electrons.<sup>31</sup> Here again we have to distinguish the cases of small and large values of  $\tau_0$ . In the case of a correlated distribution of impurities, when  $\tau_0$  of Eq. (2.38) is small and we have  $m_c \ll m_h$ , the dependence of the recombination probability on the carrier energy can be ignored.<sup>31</sup> We then find from Eq. (2.10) that<sup>29</sup>

$$\Phi_{\text{BT}}(\omega) = \frac{\rho_{0v} W_{\text{BT}}^n p \exp\{-[(E_g - \omega)/\gamma_h, s]^2\}}{p + N_v \exp[(\omega - E_g)/T] + \theta_h^n}. \quad (2.50)$$

Under these conditions free electrons have an energy of the order of  $T$  and tunnel easily and, therefore,  $\Phi_{\text{BT}}(\omega)$  is governed by the density of states in the valence band tail (2.3) multiplied by the probability of occupancy of these states (2.6). It follows from Eq. (2.50) that at moderate rates of excitation the energy

of a spectral maximum is<sup>31</sup> (see Fig. 15):

$$\omega_{m1}^{BT} = \begin{cases} E_g - T \ln \frac{N_v}{p + n_0} \equiv \omega_0 & \text{at } T < T_1 - (2.51), \\ E_g - \lambda I_a \left( \frac{2T_0}{3T} \right)^2 & \text{at } T_1 < T < T_2, \\ E_g - E_{th} + \beta T & \text{at } T > T_2 - (2.53), \end{cases} \quad (2.51)$$

$$\omega_{m1}^{BT} = \begin{cases} E_g - \lambda I_a \left( \frac{2T_0}{3T} \right)^2 & \text{at } T_1 < T < T_2, \\ E_g - E_{th} + \beta T & \text{at } T > T_2 - (2.53), \end{cases} \quad (2.52)$$

where  $\beta$  is of the order of unity. At high temperatures an additional short-wavelength maximum appears in the luminescence spectrum at

$$\omega_{m2}^{BT} = E_g - \frac{\gamma^2}{T} \text{ for } T > T_3 \quad (2.54)$$

At high rates of excitation only this maximum remains (Fig. 15). The fall of  $\Phi_{BT}(\omega)$  at long wavelengths in accordance with Eq. (2.50) reproduces the density of states in the valence band tail, whereas at short wavelengths the characteristic scale of the fall is  $T$ . (We recall that in the case of a degenerate heavily doped semiconductor discussed in Sec. 2 b the short-wavelength fall is characterized by  $\gamma_{h,s}$ .)

If the distribution of impurities is uncorrelated, i.e., if the values of  $\gamma_0$  are large, electrons recombining with holes localized in deep-tail states have to tunnel across practically unscreened Coulomb barriers. Therefore, radiative recombination is governed by electrons with energies  $\epsilon_c \sim T$ . This has the effect that in the formulas (2.51)–(2.53) for  $\omega_m^{BT}$  we have to include positive corrections but these do not alter the nature of the dependences of  $\omega_m^{BT}$  on  $T$  or the rate of excitation<sup>31</sup> (Fig. 15). The influence of tunneling on the long-wavelength edge of the luminescence spectrum at  $\omega < \omega_0$  is the more important effect. In this case the long-wavelength part of the luminescence spectrum does not reproduce  $\rho_v(\epsilon)$  or  $\alpha(\omega)$ , and cooling results in quenching at long wavelengths. One should also note that the high-temperature asymptote of the principal spectral maximum is different<sup>31</sup> for large values of  $\gamma_0$  given by Eq. (2.49) from that for small values of  $\gamma_0$  given by Eq. (2.54) (Fig. 15).

The luminescence spectrum of a strongly compensated heavily doped semiconductor may, in principle, also have a maximum (Fig. 15) associated with the recombination of free holes and localized electrons (TB transitions; see Fig. 13). However, the intensity of this maximum is low<sup>31</sup> if  $m_h \gg m_c$  because of the low probability of tunneling of holes whose mass is greater.

#### f) Transient luminescence characteristics

The time dependence of the luminescence spectrum after the end of excitation is influenced directly by the nature of the distribution of the minority carriers between the localized tail states. For example, if the distribution of holes in an  $n$ -type heavily doped semiconductor is of the quasiequilibrium type, then after the end of excitation the change in this distribution as a result of recombination reduces to a displacement of the quasi-Fermi level of holes  $F_p$  deeper into the band gap. Then, the intensity of the low-frequency luminescence should not decrease until the quasi-Fermi level  $F_p$  reaches that energy level in the valence band tail which determines the luminescence at the frequency in question (Fig. 16a). However, experimental studies

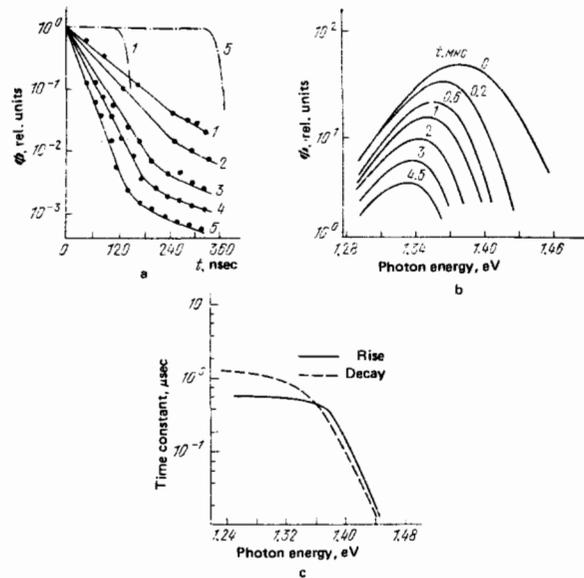


FIG. 16. Time characteristics of the photoluminescence of heavily doped and strongly compensated samples of GaAs at 77°K: a) luminescence intensity decay  $\Phi(t)$  after the end of an excitation pulse recorded for different photon energies<sup>113</sup> [1 corresponds to the photon energy 1.341 eV, 2 to 1.365 eV, 3 to 1.39 eV, 4 to 1.414 eV, and 5 to 1.439 eV, chain curves show the decay of  $\Phi(t)$  in the case of a quasiequilibrium distribution of carriers between the tail states]; b) evolution of the luminescence spectrum in time<sup>97</sup> (the numbers alongside the curves give the time in micro-seconds from the end of an exciting pulse); c) dependences of the decay and rise time constants on the photon energy.<sup>37</sup>

of the decay of the luminescence of compensated heavily doped GaAs have shown<sup>97,113,133</sup> that, irrespective of the frequency, the luminescence intensity decreases exponentially immediately after the end of excitation (Fig. 16a). This means that the luminescence intensity decreases not only at short but also at long wavelengths (Fig. 16b). It has also been found that the time constant of the decay and rise of the intensity at long wavelengths depends weakly on the frequency and that it decreases strongly at short wavelengths beginning from a certain particular frequency (Fig. 16c). Thus, different levels in the valence band tail governing the long-wavelength luminescence are deexcited independently. This shows that the distribution of holes between the tail states is not in quasiequilibrium, as first pointed out in experimental investigations.<sup>18,97,113,133</sup> The reasons for this absence of quasiequilibrium falls are discussed in detail in Sec. 2 b.

We shall now consider the decay of the luminescence emitted by an  $n$ -type weakly degenerate compensated heavily doped semiconductor ( $\mu_h < \gamma_h$ ). At low excitation rates the density of free electrons in such a semiconductor can be regarded as constant and equal to the equilibrium value  $n_0$ . Since the scatter of the electron energies is small, the luminescence decay at this frequency is governed by the change in the population  $q_h(\epsilon)$  of a group of closely spaced levels in the valence band tail. Since free holes are captured almost immediately by localized tail states after the end of excitation, we can substitute  $p=0$  in the transport equa-

tion (2.5), which gives

$$\frac{\partial q_n(\varepsilon)}{\partial t} = -\left[n_0 \tilde{W}_n(\varepsilon) + W_p N_v \exp\left(-\frac{\varepsilon}{T}\right)\right] q_n(\varepsilon). \quad (2.55)$$

If we bear in mind that in this case  $\varepsilon = E_g - \omega$  (to within  $\mu_n$  and  $kT$ ) it follows from this equation that  $\Phi(\omega, t) \sim q_n(\omega, t) \sim \exp[-t/\tau(\omega)]$ , where

$$\tau^{-1}(\omega) = n_0 \tilde{W}_n(\omega) + W_p N_v \exp\left(\frac{\omega - E_g}{T}\right). \quad (2.56)$$

The dependence  $\tau(\omega)$  observed experimentally<sup>97,113</sup> at low frequencies (Fig. 16c) can be explained<sup>31</sup> by the energy dependence of the probability of radiative transitions (Sec. 2b). The steep fall of  $\tau(\omega)$  at high frequencies (Fig. 16c) is related to the thermal release of holes from relatively shallow levels in the valence band tail, followed by their capture by deeper levels.

At high rates of excitation such that nonequilibrium electrons are degenerate, the fast decay of the short-wavelength luminescence can be due to another reason. In this case the end of excitation reduces the electron density and displaces the quasi-Fermi level toward the bottom of the conduction band, which displaces the spectral intensity maximum. Naturally, when the electron density increases so much that  $\mu_n$  becomes less than  $\gamma_n$ , the luminescence decay changes the profile and position of the spectral line (Fig. 16b) only slightly.

It is clear from Fig. 16a that the luminescence decay slows down with time. This is characteristic of strongly compensated samples<sup>113</sup> and it is of the same origin as the "frozen" photoconductivity (Sec. 2e).

## CONCLUSIONS

Our discussion of the luminescence spectra of heavily doped semiconductors is based on the assumption of given (constant) densities of free carriers, which is usual in the various problems considered in the theory of recombination.<sup>54,55,95</sup> It is of interest to determine also the relationship between the densities of electrons and holes and the rates of pumping for different types of excitation, i.e., the relationship between such densities and the current in the case of injection luminescence or the intensity of the exciting light in the case of photoluminescence. In such cases the main channel controlling the density of free nonequilibrium carriers is usually not the radiative recombination but one of the forms of nonradiative recombination. A consistent analysis of this problem in the case of excitation has not yet been made [see, in particular, the comments after Eq. (2.48)].

The theory of injection luminescence of heavily doped semiconductors based on the assumptions made in the present review is developed in Refs. 36 and 37. It has been possible to explain, from a common standpoint, the great variety of the experimentally observed specific brightness-voltage and current-voltage characteristics of light-emitting structures made of heavily doped semiconductors. The characteristic temperature  $T_3$  of Eq. (2.15), above which the distribution of carriers between localized states in the tail becomes essentially quasiequilibrium and the nature of the spectrum ceases to depend on the rate of excitation, is found to be the "demarcation" temperature also in the

case of brightness-voltage characteristics. For example, at  $T > T_3$  the dependence of the luminescence intensity on the voltage is of the thermally activated type  $\Phi \propto \exp(eV/\beta T)$  with  $\beta = 1$ , irrespective of the parameters of the light-emitting structure.<sup>36</sup> This result explains the experimental data of Refs. 7, 13, 18, 98, 105, 111, 134 whereas the usual concepts<sup>35,135</sup> indicate that, for example, in the case of a  $p-i-n$  structure we have  $\beta = 2$ . On the other hand, at low temperatures ( $T < T_3$ ) there is a greater variety of the brightness-voltage characteristics. For example, in the case when the internal quantum efficiency is close to 100%, it follows from the experimental results<sup>12,13</sup> that  $\beta = 2$  for  $p-n$  structures and  $\beta = 1.5$  for  $p-i-n$  structures in the case of interband<sup>37</sup> or impurity<sup>35</sup> recombination. In the case of low-efficiency structures the dependence of the luminescence intensity on the voltage is usually not thermally activated but is governed by the nature of the density-of-states tail. This theoretical conclusion<sup>37</sup> is also in agreement with the experimental results.<sup>7,18,98,111,134,136</sup> Since the nature of the tail determines also the form of the luminescence spectrum, there is a correlation between the brightness-voltage characteristic and the luminescence spectrum, found also experimentally.<sup>136</sup>

It should be noted that in the interpretation of the experimental results we have to bear in mind<sup>136</sup> that the nonthermally activated nature of the brightness-voltage characteristic may be associated also with tunnel radiative transitions in the region of a  $p-n$  junction of a structure made of a heavily doped semiconductor.<sup>137</sup> Moreover, the shape of the luminescence spectrum observed at temperatures  $T < T_3$  may have been influenced considerably by the inhomogeneous distribution of the injected carriers. In a comparison with the experimental results the formulas for the spectra given in the present review should be integrated with respect to the coordinate.

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