

Density of states and interband absorption of light in strongly doped semiconductors

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The electronic properties of strongly doped semiconductors (SDP) differ greatly from the properties of pure semiconductors, to which many monographs and text books have been devoted. A serious study of SDP was started about 10 years ago. The quasiclassical method, its results, and the region of applicability are discussed in detail. It is shown that this method cannot be used to describe deeply-lying fluctuation levels. This is followed by the recently developed method of optimal fluctuation, which makes it possible to find the argument of the exponential of the density of states deep in the forbidden band. Using this method, the density of states is analyzed at different relations between the semiconductor parameters and at all values of the energy for which the effective-mass method is applicable. The difference between the spectra of the majority and minority carriers is indicated. The influence exerted on the state density by the correlation in the impurity distribution is considered. A study of the structure of the fluctuation levels makes it possible to construct the theory of the interband light absorption coefficient (ILAC) at frequencies below the threshold. It is shown that the frequency dependence of the ILAC does not always duplicate the dependence of the density of states on the energy. An analysis of the experimental data indicates that the minority carriers play an important role in the formation of the "tail of the ILAC."

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1. INTRODUCTION

Modern semiconductor electronics makes extensive use of strongly doped semiconductors (SDS), the electronic properties of which differ significantly from the properties of pure semiconductors described in most monographs and text books.

A serious study of SDS started about 10 years ago. It was stimulated by the invention of a number of devices in which an important role is played by electronic states that are produced in the forbidden band under the influence of impurities. Since that time, very many original papers on this subject have been published, and by now the theory of the density of state and of interband absorption of light has reached a certain degree of completeness. Calculation methods have been developed and results have been obtained that are valid when the semiconductor parameters differ strongly from one another. Unfortunately, in the analysis of the experimental data one encounters most frequently intermediate cases, so that numerical agreement between experiment and theory cannot be expected as yet. However, an analysis of limiting cases yields a physical explanation of the phenomena and this explanation, of course, remains in force in the intermediate cases and makes it possible to gain an approximate understanding of the intermediate cases. Further development of the theory in this region will probably follow mainly the path of development of numerical calculation methods. It is clear that the analytical results obtained in limiting cases will play a very important role in this case.

The difficulty in the grasping of all the original papers lies in the fact that different authors use different approximations, without always distinctly stipulating the limits of their applicability. It is therefore necessary to exert considerable efforts to compare various

results. This leads frequently to confusion in the reduction of the experimental data. The number of review articles on this subject is extremely small (see the survey^[1] and small fragments devoted to SDS in the reviews^[2,3]). We therefore deemed it advisable to present the present-day ideas concerning the properties of the electronic states in SDS from a unified point of view.

We consider a semiconductor doped with shallow impurities (for the sake of argument, donors). The electronic states on these impurities can be investigated within the framework of the effective-mass method. We assume for simplicity that the carrier spectrum is isotropic and quadratic. Then the states localized near one isolated impurity are hydrogenlike. The energy E_0 and the radius a of the ground state are expressed in the usual manner

$$E_0 = \frac{me^4}{2\kappa^2\hbar^2}, \quad a = \frac{\hbar^2\kappa}{me^2} \quad (1.1)$$

in terms of the effective mass of the electron m and the dielectric constant κ (e is the absolute value of the electron charge).

We shall attempt to ascertain now how the electronic states are arranged at low temperature if the entire volume of the semiconductor is filled with randomly disposed donors with density N . Obviously, if the density N is low enough, then the electrons are in hydrogenlike ground states localized near individual donors, and the electron density in the conduction band decreases with temperature like $\exp(-E_0/T)$, where T is the temperature expressed in energy units. It is obvious also that the impurity density should be low enough so that the wave functions of the electrons located at neighboring donors overlap very little, i.e., the condition $Na^3 \ll 1$ must be satisfied; we shall call

this the weak-doping condition. Under this condition, the scatter of the levels of the electrons located at the impurities is small in comparison with the energy E_0 (the impurity band is narrow). With increasing impurity density, the band broadens and finally coalesces with the bottom of the conduction band.

In the case $Na^3 \gg 1$, which is customarily called the case of strong doping and to which our review is devoted, the picture of the electronic states is entirely different. It is clear that there are no states localized near individual donors. The conduction electrons that appear in the semiconductor together with the donors form a Fermi gas. The Fermi energy increases with the impurity density more rapidly than the interaction energy of the electrons with one another and with the impurities. Therefore at $Na^3 \gg 1$ the kinetic energy of the overwhelming number of electrons is large in comparison with the potential energy. Thus, in a weakly compensated SDS the electrons form an almost ideal Fermi gas. The electronic conductivity at low temperatures is of metallic character (independent of the temperature).

The Bohr radius a in semiconductors can be very large. Thus, in n -InSd the radius is $a \approx 600 \text{ \AA}$, i.e., the strong-doping condition is satisfied already at $N \approx 10^{16} \text{ cm}^{-3}$. In practice, with modern methods of purification, it is very difficult to obtain weakly doped compounds such as n -InSb or n -InAs. (Samples with small electron densities are usually compensated.)

The most important task of the SDS theory is to describe the electronic states, the energies of which lie in a region that is a forbidden band for a pure semiconductor. The electrons in such states are responsible for the operation of a large number of modern semiconductor devices, such as lasers, various spontaneous emitters, and tunnel diodes. The levels in the forbidden band result from fluctuations of the concentrations of the charged impurities and are called fluctuation levels. In fact this is the problem of the spectrum of a disordered system, but in the case of the SDS it has the following distinguishing features:

- 1) The impurity potential is of the Coulomb type, i.e., long-range.
- 2) The potential screening radius, which is determined as a rule by the electron, is larger than the average distance between impurities. This circumstance prevents us from applying to the SDS the models considered in the theory of disordered systems (see, e.g., the review by I. M. Lifshitz^[4]), in which the potential is assumed to be short-range.
- 3) From the condition $Na^3 \gg 1$ it follows that one Coulomb potential well, cut off at the average distance between the impurities, does not contain a bound state at all. The electronic states in the forbidden band are produced as a result of fluctuations that include a large number of charged impurities. The deeper the state, the lower the probability of its formation. Therefore the density of states in the SDS decreases monotonically towards the interior of the forbidden band.
- 4) The characteristic energies that determine the fall-off of the density of states are much smaller than the width of the forbidden band. The theory can therefore be constructed within the framework of the effective-mass method.

Our review consists of three parts. Chapter 2 is devoted to an exposition of the "band bending" method, which makes it possible to describe the electronic states near the unperturbed bottom of the conduction band. (By unperturbed bottom of the conduction band we understand the energy corresponding to the bottom of the band in the absence of impurities.) This method, however, is not applicable for a description of states whose energy is lower than the bottom of the unperturbed band by an amount greatly larger than the mean-square fluctuation of the bottom of the band. In this energy region, the density of states decreases towards the interior of the forbidden band exponentially, like $\exp(-\Omega(\epsilon))$, with $\Omega(\epsilon) \gg 1$. In Chap. 3 is described the optimal-fluctuation method, which makes it possible to determine the argument of the exponential that describes the tail of the density of states. The most interesting cases from the point of view of the SDS are considered by this method.

Finally, in Chap. 4, the optimal-fluctuation method is used to find the law governing the decrease of the interband light absorption coefficient at frequencies lower than the width of the forbidden band. Experimental data on light absorption are analyzed at the end of this chapter.

2. DENSITY OF STATES NEAR THE BOTTOM OF A BAND

a) Quasiclassical approximation. Bonch, Bruevich, Kane, and Keldysh, at the 1962 International Conference on Semiconductor Physics at Exeter, have independently advanced the idea that quasiclassical concepts can be used to describe the density of states of a strongly doped semiconductor.

If the potential produced by the fluctuation of the impurity density is small in comparison with the Fermi potential, then the screening of such fluctuations can be regarded in the Debye approximation. In this approximation, the Poisson equation is linearized and each charged center is screened independently of the remaining centers. It is therefore possible to assume that the potential produced by all the centers is equal to the sum of the potentials of the individual centers screened in the Debye manner.

Let V be the potential energy of a test electron in the field of impurities. Then

$$V(\mathbf{r}) = \sum_{j=1}^{\mathcal{N}} \varphi(\mathbf{r} - \mathbf{r}_j), \quad \varphi(r) = -\frac{e^2}{\kappa r} e^{-r/r_s}, \quad (2.1)$$

where

$$r_s = \frac{a}{2} \left(\frac{\pi}{3} \right)^{1/3} \frac{1}{(na^3)^{1/3}} \quad (2.2)$$

is the screening radius, \mathbf{r}_j is the radius vector of the impurity center, and the summation is carried out over all \mathcal{N} centers present in the crystal. In order not to clutter up the formulas by unnecessary summation signs, we assume that there are only attracting impurities (donors) with density N (there is no compensation). Then the neutrality condition yields therefore the electron density $n = N$. As will be shown below, at not too high degrees of compensation the generalization of the results is very simple.

We shall assume that the electrons are classical and "feel" only the potential of that point at which they are located. This means that we should calculate the density

of states in accordance with the usual formula for free electrons^[5], but we must assume that the kinetic energy K at some point r is equal to $\epsilon - V(r)$, where ϵ is the total energy, i.e., K is reckoned from the conduction-band bottom perturbed by the fluctuation potential. (For this reason, this procedure is sometimes called the method of 'bent bands'.) For the state density we obtain

$$\rho_{cl}(\epsilon) = \frac{(2m)^{3/2}}{2\pi^2\hbar^3V_0} \int V\sqrt{\epsilon - V(r)} d^3r, \quad (2.3)$$

where the integral is taken over the entire volume V_0 of the crystal, and the integrand should be regarded as equal to zero at the points $V(r) > \epsilon$. Replacing the integration over the volume by averaging over all the configurations of the impurities, we obtain

$$\rho_{cl}(\epsilon) = \frac{(2m)^{3/2}}{2\pi^2\hbar^3} \int_{-\infty}^{\epsilon} dV [V\sqrt{\epsilon - V} F(V)], \quad (2.4)$$

where $F(V)$ is the distribution function of the potential energy. By definition we have

$$F(V) = \int \frac{d^3r_1}{V_0} \int \frac{d^3r_2}{V_0} \dots \int \frac{d^3r_{\mathcal{N}}}{V_0} \delta\left(V - \sum_{j=1}^{\mathcal{N}} \varphi(r - r_j)\right). \quad (2.5)$$

We calculate $F(V)$ by the Markov method (see^[6]). To this end, we substitute in (2.5) the identity

$$\delta\left(V - \sum_{j=1}^{\mathcal{N}} \varphi(r - r_j)\right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{it\left(V - \sum_{j=1}^{\mathcal{N}} \varphi(r - r_j)\right)}. \quad (2.6)$$

We then obtain

$$F(V) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{iVt} P(t), \quad (2.7)$$

where

$$P(t) = \left[\int \frac{d^3r}{V_0} e^{-i\varphi(r)t} \right]^{\mathcal{N}} = \left[1 + \frac{f(t)}{V_0} \right]^{\mathcal{N}}, \quad (2.8)$$

and

$$f(t) = \int d^3r (e^{-i\varphi(r)t} - 1). \quad (2.9)$$

Changing over in (2.8) to the limit as $\mathcal{N} \rightarrow \infty$, $V_0 \rightarrow \infty$, and $\mathcal{N}/V_0 \rightarrow N$, we obtain ultimately

$$F(V) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{iVt + Nf(t)}. \quad (2.10)$$

Assuming t to be small, we now expand the exponential in (2.9). We then obtain

$$Nf(t) = i\Gamma t - (\gamma^2 t^2/4), \quad (2.11)$$

where

$$\Gamma = -N \int \varphi(r) d^3r = 4\pi (e^2/\kappa r_s) N r_s^3 \quad (2.12)$$

and

$$\gamma^2 = 2N \int \varphi^2(r) d^3r = 4\pi (e^4/\kappa^2 r_s^2) N r_s^3. \quad (2.13)$$

The first term of (2.11) describes the shift of the bottom of the band as a result of the average potential of the charged impurities. This term is exactly compensated for by the potential of the electrons, and will be disregarded in the calculations that follow. Substituting the second term of (2.11) in (2.10), we obtain the Gaussian distribution

$$F(V) = \frac{1}{\sqrt{\pi\gamma}} e^{-V^2/\gamma}. \quad (2.14)$$

The physical meaning of the rms potential γ is very simple. The rms fluctuations of the number of impurities in the volume r_s^3 is of the order of $(N r_s^3)^{1/2}$, and

the potential energy of the electron in the field of such a fluctuation is $(e^2/\kappa r_s)(N r_s^3)^{1/2} \approx \gamma$.

It is easy to show that our expansion in (2.9) is valid if

$$N r_s^3 \gg 1 \text{ and } V \ll (e^2/\kappa r_s) N r_s^3. \quad (2.15)$$

The meaning of these inequalities is perfectly obvious. Since the main contribution to $F(V)$ is made by fluctuations with dimension r_s , it follows from the first inequality that the average number of particles in a fluctuation should be large. Representing V in the form $V = (e^2/\kappa r_s)\Delta\mathcal{N}$, where $\Delta\mathcal{N}$ is the excess number of particles in the fluctuations, we see that the second condition signifies $\Delta\mathcal{N} \ll N r_s^3$, i.e., the excess number of particles should be much smaller than the average. Thus, the inequalities (2.15) are the usual conditions of the applicability of Gaussian statistics to the fluctuations of the dimension r_s .

Substituting (2.14) in (2.4), we obtain the principal result of Kane^[7] and Keldysh^[8]:

$$\rho_{cl} = \frac{(2m)^{3/2}}{2\pi^{5/2}\hbar^3\gamma} \int_{-\infty}^{\epsilon} V\sqrt{\epsilon - V} e^{-V^2/\gamma^2} dV. \quad (2.16)$$

At $\epsilon > 0$ and $\epsilon \gg \gamma$ we have

$$\rho_{cl} = \rho_0 - \frac{(2m)^{3/2}\gamma^2}{32\pi^{5/2}\hbar^3 e^{3/2}}, \quad (2.17)$$

where

$$\rho_0 = \frac{(2m)^{3/2}\sqrt{\epsilon}}{2\pi^2\hbar^3},$$

from which we see that in this case ρ_{cl} is close to the density of states ρ_0 of the free electrons. At $\epsilon < 0$ and $|\epsilon| \gg \gamma$ we have

$$\rho_{cl}(\epsilon) = \frac{m^{3/2}\gamma^{1/2}}{4\pi^2\hbar^3} \left(\frac{\gamma}{\epsilon}\right)^{3/2} e^{-\epsilon^2/\gamma^2}. \quad (2.18)$$

Thus, the density of states decreases exponentially in the interior of the forbidden band. The integral (2.16) is tabulated in^[7,9]. The corresponding plot is shown in Fig. 1.

It is easy to verify that at $Na^3 \gg 1$ the Fermi energy $\mu_0 = (3\pi^2)^{2/3}(\hbar^2/2m)N^{2/3}$ is much larger than γ , i.e., the Fermi level is located in the energy region where the density of states is close to ρ_0 . It is this circumstance that enables us to regard the fluctuation screening as Debye screening.

Measurement of the Moss-Burstein threshold, and also other experiments, offer evidence that the Fermi energy in the SDS is somewhat lower than μ_0 . This is caused by the nonideal character of the electron gas. Let $\mu = \mu_0 - \mu_{ee} - \mu_{ei}$, where μ_{ee} and μ_{ei} are corrections due to the interaction of the electron with one another and with the impurities. The main correction is due to the exchange interaction of the electrons. According to^[10] we have

$$\mu_{ee} = \frac{e^2}{\pi} \frac{\sqrt{2m\mu_0}}{\hbar}. \quad (2.19)$$

The correction μ_{ei} can be obtained with the aid of (2.16):

$$\mu_{ei} = \frac{1}{8} \frac{\gamma^2}{\mu_0} \quad (2.20)$$

It describes the lowering of the Fermi level as a result of the tail of the density of states.

A generalization of the results to the case of a compensated semiconductor entails no special difficulties^[9]

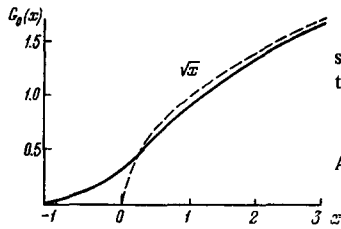


FIG. 1. Quasiclassical density of states. Solid curve—plot of the function

$$G_0(x) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^x e^{-y^2} (x-y)^{1/2} dy.$$

According to (2.16) we have

$$\rho_{cl}(\epsilon) = \frac{\sqrt{2}m^{3/2}\hbar^{1/2}}{\pi^2\hbar^3} G_0\left(\frac{\epsilon}{\gamma}\right).$$

if it is assumed, as before, that the single-electron approximation is applicable and that the impurities are screened in Debye fashion. In addition to positive donors, there are also in this case negative acceptors with density N_A and the electron density is $n = N - N_A$. The obvious generalization consists in the fact that it is necessary to replace N in the rms potential γ (2.13) by the total density $N + N_A$ of the charged centers. Since $N < N + N_A < 2N$, we can ignore this circumstance in the estimates. What is much more important is that in the screening radius r_S (2.2) and in the Fermi energy μ_0 it is necessary to replace N by the electron density n , which can be much smaller than N . With decreasing n , the screening radius r_S and the characteristic value of the potential energy γ increase, while the Fermi energy μ_0 decreases. It is obvious that the Debye approximation is applicable if

$$\alpha \equiv \gamma/\mu_0 \approx (N/n)^{3/4}/(Na^3)^{-1/4} \ll 1. \quad (2.21)$$

This condition limits the applicability of the theory developed above to strongly compensated semiconductors. The case $\alpha > 1$ is considered in^[11], but its description is beyond the scope of our review.

b) Region of applicability of the quasiclassical approximation. It may seem at first glance that formula (2.4) and the corrections to it can be obtained by expansion in terms of Planck's constant \hbar , assuming the potential of the impurities to be a smooth one. Such an expansion for the partition function is described in the text book of Landau and Lifshitz^[12]. Formula (2.4) is indeed obtained in the zeroth approximation (it is purely classical), and $F(V)$ is not necessarily expressed by formula (2.14). It can be shown^[13], however, that the ratio of the correction term of the expansion, which takes into account the gradients of the potential, to the zeroth term near the bottom of the band is of the order of a/r_S . This result can be easily understood. The considered potential (2.1) is a superposition of the screening of Coulomb wells. The condition $a/r_S \ll 1$ means that each such well contains many bound states. It is under this condition that the expansion indicated above is valid. It follows, however, from the conditions $Na^3 \gg 1$ and $\alpha \ll 1$ (2.21) that $a/r_S \gg 1$. Thus, the expansion in terms of the derivatives of the potential cannot be used in the case of SDS.

A rigorous derivation of formula (2.16) for SDS was first obtained by Keldysh^[6] by a diagram technique. This derivation is not an expansion in terms of \hbar , and is based on an ultraquantum property, namely the absence of a level in a strongly screened Coulomb well. Later on, in^[14], a special diagram technique was developed, in which the large-scale fluctuations of the impurity potential were taken into account in all orders of perturbation theory, but in a quasiclassical manner, and the small-scale fluctuations were taken into account quantum-mechanically, but by perturbation theory. Unlike ordinary perturbation theory, which is applicable

only when $\epsilon \gg \gamma$, the modified theory is applicable at all positive and not too large negative energies. The Green's function obtained in the zeroth approximation of this theory leads to formula (2.16), and the next approximations yield corrections to it. With the aid of such a theory it is easy to obtain the expansion parameter and the region of applicability of (2.16). We present here only qualitative arguments that lead to the results of^[14].

As seen from (2.13), the main contribution to the rms potential γ is made by fluctuations of the scale r_S . Typical potential wells have a dimension r_S and a depth γ . The energy of the ground state in the well is higher than the bottom of the well by an amount on the order of $E_S = \hbar^2/mr_S^2$. The overwhelming majority of the states in this potential can be described quasiclassically if $\gamma \gg E_S$. This is the principal condition for the applicability of the developed theory. As shown in^[14], the expansion leading to (2.16), is based on the relation

$$\left(\frac{E_S}{\gamma}\right)^{1/2} = \frac{1}{(Na^3)^{1/24}} \left(\frac{n}{N}\right)^{5/24}. \quad (2.22)$$

This parameter, of course, is very poor. (According to (2.21), the ratio n/N cannot be very small.) Nonetheless, expansion in terms of this parameter seems to us to be the only possible analytic approach to the problem of the density of states near the bottom of the band, and makes it possible, in any case, to understand the physical nature of the electronic states. This in fact constitutes the main significance of the method of the bent bands.

However, the condition $(E_S/\gamma)^{1/2} \ll 1$ is not sufficient if one deals with the region $\epsilon < 0$, $|\epsilon| \gg \gamma$, where the density of states is exponentially small. In this region the main contribution to $\rho(\epsilon)$ is made by wells with depths V very close to ϵ . Indeed, in the integral (2.16) the important role in this case is played by the values

$$\epsilon - V \approx \gamma^2/|\epsilon|. \quad (2.23)$$

Thus, the kinetic energy $K = \epsilon - V$ of the considered states decreases with increasing $|\epsilon|$.

We now recall the small-scale fluctuations. At a specified kinetic energy K , the fluctuations having a larger scale than the wavelength \hbar/\sqrt{mK} can be regarded classically. Fluctuations of smaller scale average out over the wavelength of the electron. The shift of the electron level to which the small-scale fluctuations lead can be estimated by calculating the rms potential of these fluctuations. We introduce the quantity $\gamma(R)$, which we define as the rms potential $\langle V^2 \rangle^{1/2}$, and the potential of each individual well $\varphi(r)$ ($V = \sum_j \varphi(r - r_j)$) will be regarded as cut off at a distance

$R \ll r_S$. Then

$$\gamma^2(R) = 2N \int_{|r| < R} \varphi^2(r) d^3r \approx \frac{e^4 NR}{x^2}. \quad (2.24)$$

The energy shift of an electron having a kinetic energy K , due to nonclassical fluctuations, can be estimated by replacing R in (2.24) by the wavelength \hbar/\sqrt{mK} . The quantity γ_K obtained in this manner increases with decreasing K . We introduce the energy K_c , defined by

$$K_c = \gamma_{K_c} \quad \text{or} \quad K_c = E_0 (Na^3)^{2/5}. \quad (2.25)$$

For electrons having a kinetic energy $K \gg K_c$, the po-

tential $V(r)$ can be regarded as classical, since the energy shift occurring as a result of small-scale fluctuations of γK , which cannot be taken into account classically, is small in comparison with K . Since $K_C > E_S$, the minimum value of the kinetic energy at which the quasiclassical description is applicable is K_C . Substituting in the left-hand side of (2.23) the quantity K_C in place of $\epsilon - V$, we obtain the energy $\epsilon_0 = \gamma^2/K_C$, below which formula (2.16) does not hold. According to (2.18), at $\epsilon < 0$, $|\epsilon| \gg \gamma$ we have $\rho(\epsilon) \sim \exp(-\epsilon^2/\gamma^2)$. Since $\epsilon_C/\gamma = (Na^3)^{1/60}(N/n)^{1/12} \approx 1$, the condition $\epsilon > \epsilon_C$ means in practice that in the region where the density of states is exponentially small the quasiclassical approach cannot be used, and new ideas and methods are necessary to describe this region. This is the subject of the next chapter of this review.

3. DEEP TAIL OF DENSITY OF STATES

a) The optimal-fluctuation method. Halperin and Lax^[15,16], Zittartz and Langer^[17], and I. M. Lifshitz^[18] have proposed a brilliant method, which we shall call the optimal-fluctuation method, of determining the law of exponential decrease of the density of states in the region of the tail. The gist of this method reduces to the following. Assume that the radius of the wave function of the fluctuation level is larger than the average distance between impurities in the fluctuation. (In the SDS this is always the case, since $r_S < a$ and one impurity center does not produce a bound state at all.) Then the quantum-mechanical averaging smooths out the discreteness of the charge of the individual impurities and the fluctuation can be characterized by a smooth function of the coordinates $f(\mathbf{r})$, which represents the deviation of the impurity concentration from the mean value. To find the state density $\rho(\epsilon)$ it is necessary to sum the contributions from all the impurity configurations, i.e., from all the potential wells that produce electronic levels with specified energy ϵ . In the energy region of interest to us, all these probabilities are exponentially small and the indicated sum is determined by the contribution of the most probable configurations. We represent the fluctuation probability $f(\mathbf{r})$ in the form $\exp(-\Omega\{\tilde{f}_\epsilon\})$. If we find the most probable fluctuation \tilde{f}_ϵ from among all the fluctuations producing the level ϵ , then we can assert that the density of states decreases with ϵ like $\exp(-\Omega\{\tilde{f}_\epsilon\})$. When determining \tilde{f}_ϵ it suffices to consider only those fluctuations in which the level with energy ϵ is the lowest, since the probability of a fluctuation in which this level is an excited state is undoubtedly smaller.

The optimal-fluctuation method in the form in which we described it here does not yield the pre-exponential factor in the expression for the density of states, but it does make it possible to determine the principal term in the argument of the exponential, i.e., $\ln[\rho(\epsilon)/\rho(0)]$. In practice it is just this quantity which is measured in the experiment.

Of course, the problem of calculating the pre-exponential factor turns out to be much more complicated. As in the usual saddle-point method, it is necessary to take into account states that are close to extremal. In addition, it is necessary to take into account the translational invariance, i.e., the fact that the localized state can arise at any point of coordinate space.

An approximate method of calculating the pre-expo-

ponential factor was proposed by Halperin and Lax^[15]. They proposed that the wave functions of all states of a given energy produced on the fluctuations close to the extremal fluctuation coincide with the extremal wave function. It was natural to compare the result obtained by them for one-dimensional "white noise" with the asymptotic form of the exact solution that holds in this case. The difference between the pre-exponential factors was by $1/\sqrt{5}$ times. In a second paper^[16], the authors proposed a method of introducing in their approximation corrections that greatly decrease the indicated discrepancy.

Simultaneously with the first paper by Halperin and Lax, Zittartz and Langer^[17] also published a paper devoted to a determination of the asymptotic density of states in a region whose probability is exponentially small. They considered in that paper a potential of the white-noise type (in the case of one, two, and three dimensions). They obtained an exact result that differed from the result of Halperin and Lax by a number in the pre-exponential factor. This number itself can be obtained only in the one-dimensional case, where the result of Zittartz and Langer coincides with the asymptotic form of the exact solution. In the three-dimensional case, a rather complicated procedure was proposed to find this number.

I. M. Lifshitz^[18] considered the case when the potentials of the impurity centers overlap little (the effective radius is of the order of the minimal distance between the centers). This makes it possible to make a very important mathematical simplification, namely, assume that the potential is locally connected with the concentration $f(r)$. In the SDS, however, as a rule, this cannot be done, since the screening radius is larger than the average distance between the impurities. Therefore, as will be shown below, the state density in SDS differs significantly from that obtained by I. M. Lifshitz, although the idea of the "extremal fluctuation" is quite fruitful also in this case.

Halperin and Lax performed their calculations directly for semiconductors. They considered, however, only the case of Gaussian statistics, and therefore the results are applicable to fluctuation levels that are not very deep.

Shklovskii and the author^[19,20] considered a region where Gaussian statistics are not applicable. In addition, a simple method was developed in^[19] to determine approximately the optimal fluctuations and the state density. In this method it is assumed that the fluctuations have the form of uniformly charged spheres. The sphere is characterized by two parameters—the radius R and the total excess charge eZ . One of these parameters is chosen such that the energy of the ground state of the electron in the potential produced by such a fluctuation is equal to the specified value ϵ , and the second parameter is varied to obtain the optimal fluctuation. It is easily seen that in such a calculation we lose only numerical coefficients that depend on the true shape of the optimal fluctuation. The simplicity of the method enables us to analyze easily the possible cases and to compare their classification^[19]. This method is developed in the next section (b), and is used to investigate the spectrum of the majority carriers in the SDS. In Sec. (c) we obtain the exact distribution of the impurities in the optimal fluctuation and the numerical coefficients that have been left out from Sec. (b). In Sec. (d)

we consider the spectrum of the minority carriers. The distribution of the impurities in Secs. (b)–(d) is assumed to be uncorrelated. In Sec. (e) we show that the correlation connected with the repulsion of the charged impurities, a correlation that arises when the sample is prepared, greatly influences the asymptotic form of the density of states as a function of energy.

b) Uniformly charged sphere approximation. Spectrum of majority carriers. The fluctuation levels in the forbidden band can result from the clustering of attracting impurities or from rarefaction of repelling impurities. We start with only attracting impurities. We assume that the fluctuations are homogeneous spherical impurity clusters of radius R . We assume also that the impurity distribution is random. Then the probability that k impurities will fall in the volume containing on the average \bar{k} impurities is given by the Poisson formula

$$W = (\bar{k})^k e^{-\bar{k}} / k! \quad (3.1)$$

Assuming that $k \gg 1$ and $\bar{k} \gg 1$, and retaining the principal term of the probability logarithm, we obtain

$$\ln W = k \ln(\bar{k}/k) + k - \bar{k}. \quad (3.2)$$

The considered cluster contains on the average $\bar{k} = NR^3$ impurities. (In the description of this method we shall not write down the numerical coefficients, since this would mean an exaggeration of the accuracy. The expression for \bar{k} , as well as the equations that follow, should be taken only as order-of-magnitude estimates.) We represent k in the form

$$k = Z + NR^3, \quad (3.3)$$

where Z is the excess number of impurities in the fluctuation. Substituting k and \bar{k} in (3.2), we obtain the probability of the fluctuations as a function of R and Z :

$$\ln W(R, Z) = (Z + NR^3) \ln \frac{NR^3}{Z + NR^3} + Z. \quad (3.4)$$

Our problem is to obtain with the aid of the Schrödinger equation the energy of the ground state $\epsilon(R, Z)$ in a potential produced by a sphere with parameters R and Z . Since the characteristic dimension of the wave function of the ground state turns out to be much larger than the average distance between the impurities, the charge can be regarded as distributed over the considered sphere. Finding $\epsilon(R, Z)$, we express Z in terms of R and ϵ and, substituting in (3.4), we obtain the probability $W(R, \epsilon)$ that a homogeneous cluster of radius R produces an electronic state with energy ϵ . Further, we obtain $R = r_{\max}$, at which $\ln W(R, \epsilon)$ has an absolute maximum at a fixed energy. Deep in the forbidden band, where the density of states $\rho(\epsilon)$ is very small, and the number of impurities in the cluster is large, this maximum can be regarded as sharp, so that

$$\ln[\rho(\epsilon)/\rho(0)] = \ln W(r_{\max}, \epsilon). \quad (3.5)$$

This is the calculation scheme.

We introduce an auxiliary function $W(R, V)$ that defines the probability that an impurity cluster of radius R produces a well whose maximum depth is V . The potential energy V , like the energy electron ϵ , will be reckoned everywhere in this chapter downward from the unperturbed bottom of the conduction band. Then, if $R \ll r_s$, we have

$$V = (e^2/\kappa R) Z \quad (R \ll r_s). \quad (3.6)$$

(We take into account only the fluctuation potential produced by the excess impurities. The average potential of the donors is cancelled by the electrons.) If $R \gg r_s$, then a contribution to the potential is made not by all the impurities of the cluster, but only by those located at a distance smaller than the effective radius r_s . The concentration of the excess impurities is Z/R^3 , and their number in the effective radius is $(Z/R^3)r_s^3$. We therefore obtain in place of (3.6)

$$V = (e^2/\kappa r_s) (r_s^3/R^3) Z \quad (R \gg r_s). \quad (3.7)$$

Expressing Z in terms R and V with the aid of (3.6) and (3.7) and substituting in (3.4), we obtain $\ln W(R, V)$.

The auxiliary function $W(R, V)$ has a certain bearing on the sought function $W(R, \epsilon)$. Indeed, it is easy to imagine that the potential well produced by a uniformly charged sphere has an electron level ϵ close to the potential energy at the center of the sphere V , if $V \gg \hbar^2/mR^2$. Therefore at $R > r_q = \hbar/\sqrt{mV}$ we can obtain $\ln W(R, \epsilon)$ from $\ln W(R, V)$ by simply replacing V by ϵ . At $R \lesssim r_q$ it is necessary to substitute in (3.4) the function $Z(R, \epsilon)$ obtained by quantum-mechanical means.

In this and succeeding chapters we shall study the spectrum of the majority carriers in a strongly doped and weakly compensated semiconductor (for the sake of argument, n-type). As shown in Chap. 2, at $\epsilon < \epsilon_c$ the density of states is expressed by the quasiclassical formula (2.16). Since, strictly speaking, $\epsilon_c > \gamma$, it is obvious that the argument of the exponential, obtained by the optimal-fluctuation method at not too high energies, should coincide with the exponent in formula (2.18).

We introduce a length $r_2 = (V\kappa/Ne^2)^{1/2}$ with a ratio $r_2/r_s = (V/\Gamma)^{1/2}$, where $\Gamma = (e^2/\kappa r_s) Nr_s^3$. According to (2.12), Γ is the average potential energy produced by the donors. Since $\Gamma > \gamma$, the ratio r_2/r_s can be arbitrary in the region where the density of states is exponentially small. A plot of the function $\ln W(R, V)$ at $V < \Gamma$ and $V > \Gamma$ is shown schematically in Fig. 2.

We consider first the case $V < \Gamma$. It is easy to verify that the region $R > r_2$ in Fig. 2a corresponds to Gaussian statistics. Indeed, the condition for the applicability of Gaussian statistics is $Z \ll NR^3$. If $R < r_s$, then, using (3.6), we obtain

$$\frac{Z}{NR^3} = \frac{V}{(e^2/\kappa R)NR^3} = \left(\frac{r_2}{R}\right)^2. \quad (3.8)$$

At $R > r_2$ we have

$$\ln W = -Z^2/NR^3. \quad (3.9)$$

Substituting (3.6) and (3.7) in (3.9), we obtain

$$\ln W = -\frac{V^2}{[(e^2/\kappa R)(NR^3)^{1/2}]^2} \quad (r_2 < R < r_s) \quad (3.10)$$

and

$$\ln W = -\frac{V^2 R^3 \kappa^2}{e^4 N r_s^4} \quad (R > r_s). \quad (3.11)$$

Thus, at $R > r_2$ the function $\ln W(R, V)$ increases with R up to $R = r_s$, and then decreases, as shown in Fig. 2a. The decrease of $\ln W(R, V)$ at $R > r_s$ is perfectly understandable. An increase of the radius R of the sphere beyond the limits of the effective radius r_s is meaningless, since the potential of the peripheral impurities does not reach the center in any case. Thus, we have shown that the function $\ln W(R, V)$ has a relative maximum at the point $R = r_s$. From the inequality

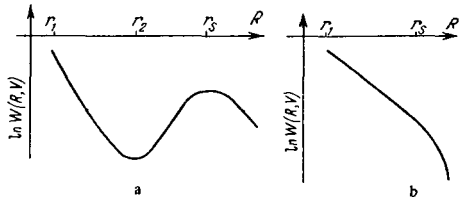


FIG. 2. Logarithm of the probability of producing a potential well of depth V by a cluster of radius R , as a function of R at $V < \Gamma$ (a) and $V > \Gamma$ (b).

$r_q/r_s = (\gamma/V)(E_s/\gamma)^{1/2} < 1$ it follows that this maximum is located in the region $R > r_q$, i.e., where the energy of the ground state ϵ coincides with the bottom of the well V . Then, in accordance with (3.5), we substitute $R = r_s$ in (3.10) or (3.11) and obtain the contribution made to the density of states by the just-obtained maximum

$$\ln |\rho(\epsilon)/\rho(0)| = -\epsilon^2/\gamma^2. \quad (3.12)$$

This formula coincides with the result (2.18) of the quasiclassical theory but, as we shall see, it has a much wider range of applicability^[19].

As seen from Fig. 2, the maximum at $R = r_s$ exists and formula (3.12) takes place only at $\epsilon < \Gamma$. Substituting $R = r_s$ in (3.8), we verify that at $V = \Gamma$ the fluctuations in a well of dimension r_s cease to be Gaussian. It is easy to show that values of V larger than Γ can in general not be obtained with the aid of Gaussian fluctuations (there is no Gaussian section at all on the curve of Fig. 2b). However, even at $\epsilon < \Gamma$ the fluctuations lying to the left of the minimum on Fig. 2a may turn out to be more probable than the fluctuations with $R = r_s$. To this end it is necessary (but not sufficient) to satisfy at $V = \epsilon$ the inequality $r_q < r_2$. Then $\ln W(R, \epsilon)$ increases with decreasing R down to $R \approx \hbar/\sqrt{m\epsilon}$.

At $R \ll r_2$, taking (3.8) into account, we obtain from (3.4)

$$\ln W = -Z \ln(Z/NR^3). \quad (3.13)$$

Substituting (3.6) in (3.13), we get

$$\ln W(R, V) = -\frac{VR\kappa}{e^2} \ln \frac{V\kappa}{2^2 NR^2}. \quad (3.14)$$

The function (3.14) decreases with decreasing R , as is indeed shown in Fig. 2a. At the same time, Z decreases to unity at $R = r_1 \equiv u^2/V\kappa$. It is clear, however, that if $V > E_0$, the well remains of the quantum type (it does not contain a bound state) at much larger values of R than r_1 . Indeed, $r_1/r_q = (E_0/V)^{1/2} < 1$.

It is easy to visualize the function $\epsilon(R, Z)$ at $R \ll \hbar/\sqrt{m\epsilon}$. In this case the fluctuation represents an almost pointlike nucleus of the atom, the lowest term of which realizes the energy ϵ . With the correction for the non-pointlike nature of the nucleus, we have

$$\epsilon = Z^2 E_0 \left(1 - \frac{R^2}{(a/Z)^2}\right). \quad (3.15)$$

Thus, at $R \ll \hbar/\sqrt{m\epsilon}$ the ground-state energy ϵ never coincides with the maximal depth V (3.6), which tends to infinity as $R \rightarrow 0$, but tends to a constant value $Z^2 E_0$.

Inverting (3.15), we obtain

$$Z = \sqrt{\frac{\epsilon}{E_0}} \left(1 + \frac{R^2}{a^2} \frac{\epsilon}{E_0}\right), \quad R \ll \frac{\hbar}{\sqrt{m\epsilon}} \approx a \sqrt{\frac{E_0}{\epsilon}}. \quad (3.16)$$

Substituting (3.16) in (3.13) we see that $\ln W(R, \epsilon)$

$\rightarrow -\infty$ as $R \rightarrow 0$. Inasmuch as at $R \gg \hbar/\sqrt{m\epsilon}$ we can use for $\ln W(R, \epsilon)$ formula (3.14), in which we can put $V = \epsilon$, this means that $\ln W(R, \epsilon)$ has a second maximum (Fig. 3). It is determined by the competition between the combinatorial logarithm in (3.13), which shows that "friable" nuclei are more probable on the one hand, and the correction for the fact that the nucleus is not pointlike in (3.16), which indicates that pointlike nuclei can ensure the specified energy with decreasing Z , on the other. Since the correction for the non-pointlike nature enters in (3.3) in power-law fashion, it has a stronger influence and the optimal nucleus is pointlike ($r_{\max} < \hbar/\sqrt{m\epsilon}$). To determine r_{\max} it suffices therefore to substitute (3.16) in (3.13) and obtain the maximum with respect to R . As a result we have for the optimal fluctuation

$$r_{\max} \approx \frac{\hbar}{\sqrt{m\epsilon}} \frac{1}{\sqrt{\ln \left[\left(\frac{\epsilon}{E_0}\right)^2 \frac{1}{Na^3} \right]}}. \quad (3.17)$$

It was assumed in the derivation that the argument of the logarithm in (3.17) is much larger than unity. At energies for which the density of states is determined by the considered maximum ($\epsilon > E_1$; see below), this condition is satisfied.

Thus, the dimension of the optimal cluster is small in comparison with its Bohr radius, i.e., this cluster represents almost a pointlike nucleus of the atom.

Substituting $Z = \sqrt{\epsilon/E_0}$ and r_{\max} from (3.17) in (3.13), we obtain^[20]

$$\ln \frac{\rho(\epsilon)}{\rho(0)} = -V \sqrt{\frac{\epsilon}{E_0}} \ln \left[\left(\frac{\epsilon}{E_0}\right)^2 \frac{1}{Na^3} \right], \quad (3.18)$$

where

$$D(\epsilon) \approx \left\{ \ln \left[\left(\frac{\epsilon}{E_0}\right)^2 \frac{1}{Na^3} \right] \right\}^{3/2}. \quad (3.19)$$

From a comparison of (3.18) and (3.12) we see that (3.18) holds at $\epsilon > E_1$ and (3.12) at $\epsilon < E_1$, where

$$E_1 = \frac{\gamma^{4/3}}{E_0^{1/3}} \left\{ \ln \left[\left(\frac{\gamma}{E_0}\right)^2 \frac{1}{Na^3} \right] \right\}^{2/3}. \quad (3.20)$$

It is easy to verify that $E_1 < \Gamma$ in this case. If $\epsilon > \Gamma$, as already mentioned, the maximum at $R = r_s$ vanishes, and the arguments pertaining to the maximum at $R = R_{\max}$ (3.17) do not change at all. Thus, formula (3.18) is valid for all energies $\epsilon > E_1$ within the limits of the effective-mass method. Let us discuss now the assumptions made in the derivation of this formula.

In the derivation of (3.18) we have regarded Z as a continuous variable. This is true if the width of the maximum of the function $\ln W(Z, \epsilon)$ with respect to the variable Z is large in comparison with unity. It is easy to verify that this takes place if

$$\left(\frac{\epsilon}{E_0}\right)^{1/4} > \ln \left[\left(\frac{\epsilon}{E_0}\right)^2 \frac{1}{Na^3} \right]. \quad (3.21)$$

Formula (3.18) was obtained in the uniformly charged sphere approximation. The dimension of the optimal fluctuation was determined without taking into account the numerical factors, since they actually depend on the distribution of the density with respect to the fluctuation.

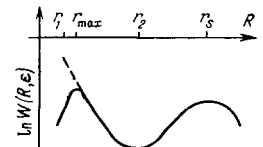


FIG. 3. Logarithm of probability of producing an electronic state of energy ϵ by a cluster of radius R as a function of R ($E_s < \epsilon < \Gamma$).

However, the statement $r_{\max} < a/Z$ does not depend on the made approximation. Therefore the factor preceding the logarithm in (3.18) contains no additional numbers at all, as is indeed confirmed by the theory developed in Sec. (c), in which the true distribution of the charge in the fluctuation is determined and the exact function $D(\epsilon)$ is obtained. Furthermore, within the framework of the effective-mass method the factor preceding the logarithm does not depend on the spectrum (if E_0 is taken to mean not (1.1) but the exact value of the ground-state energy). Indeed, the form of this factor is a consequence of the fact that $\epsilon \sim Z^2$, but this is always the case when the Hamiltonian is a quadratic form of the momentum components.

The entire reasoning of this chapter is based on the one-electron approximation and on the assumption of Debye screening of the impurities. Actually, however, we needed the Debye screening only in the derivation of (3.12). Inasmuch as $E_1 < \mu_0$ in a weakly compensated semiconductor, where μ_0 is the Fermi energy, the Debye screening assumption imposes no limitations on the region of applicability of (3.12). As to formula (3.18), allowance for electron-electron interaction does not affect it also when $\epsilon > \mu_0$. The formation considered by us constitutes a multielectron atom, the lowest term of which realizes the required energy ϵ . However, as is well known^[21], the outer electrons alter the energy of this term little if the charge of the nucleus is large.

Thus, (3.18) is an asymptotic expression for the state density at high energies within the framework of the effective-mass method. It is important, however, that we have assumed that the impurities are randomly distributed. As will be shown in Sec. (e), correlation effects (if they exist) alter the asymptotic form of the state density. To use the Poisson formula it is also necessary that the average distance between the impurities and the clusters be much larger than the lattice constant. It is easy to verify, however, that the energies at which this condition is violated are comparable with the width of the forbidden band.

We have thus considered the density of states of the majority carriers in strongly doped and weakly compensated semiconductors, and have proved that it is described by formulas (3.12) and (3.18), which become equal at $\epsilon \approx E_1$.

c) **Exact distribution of impurities in optimal fluctuations.** 1) Derivation of fundamental equations. In the preceding section we have carried out a qualitative analysis in which it was assumed that the fluctuations constitute homogeneously charged spheres that differ from one another only in the radius and in the charge density. We proceed now to the development of a rigorous theory with which to obtain the true form of the optimal fluctuations.

We introduce the function $f(\mathbf{r}) = N(\mathbf{r}) - N$, where $N(\mathbf{r})$ is the impurity density at the point \mathbf{r} averaged over a volume larger than N^{-1} . We obtained the probability of the fluctuation $f(\mathbf{r})$, assuming that there is no correlation in the impurity distribution. To this end we consider a volume element ΔV small enough to regard $N(\mathbf{r})$ as constant within it, but containing a large number of impurities $\mathcal{N} = N(\mathbf{r})\Delta V \gg 1$. To calculate the number of states we assume that the impurities can be located only at the lattice sites, and that the concentration of these sites is $p \gg N(\mathbf{r})$. Let us find a number of ways in which it is possible to distribute \mathcal{N} impurities

over the lattice sites located in the volume ΔV . The number of sites is $\mathcal{P} = \mathcal{P}\Delta V$, and the sought number of methods $\Gamma_{\Delta V}$ is the number of combinations of \mathcal{P} taken \mathcal{N} at a time:

$$\Gamma_{\Delta V} = \mathcal{P}!/\mathcal{N}!(\mathcal{P} - \mathcal{N})!. \quad (3.22)$$

For the entropy of the volume ΔV we obtain

$$S_{\Delta V} = \ln \Gamma_{\Delta V} = \mathcal{N} \ln (\mathcal{P}e/\mathcal{N}). \quad (3.23)$$

We now introduce the entropy density

$$S_{\Delta V} = \sigma(\mathbf{r}) \Delta V, \quad \sigma(\mathbf{r}) = N(\mathbf{r}) \ln (pe/N(\mathbf{r})). \quad (3.24)$$

The total entropy of the crystal, which has a volume V_0 , is

$$S = \int_{V_0} d^3r \sigma(\mathbf{r}). \quad (3.25)$$

Let us obtain the entropy of an impurity distribution such that a fluctuation $f(\mathbf{r})$ generally speaking comparable with $N(\mathbf{r})$, takes place in a certain volume V constituting a negligible fraction of V_0 , and in the remaining part of the volume we have $f(\mathbf{r}) \ll N$. From the law of conservation of the number of particles we have

$$\int_{V_0-V} f(\mathbf{r}) d^3r = - \int_V f(\mathbf{r}) d^3r. \quad (3.26)$$

The entropy of such a fluctuation is

$$S = \int_V (N+f) \ln \frac{pe}{N+f} d^3r + (V_0-V) N \ln \frac{pe}{N} + \int_{V_0-V} \left(\frac{d\sigma}{dN(\mathbf{r})} \right)_{N(\mathbf{r})=N} f d^3r. \quad (3.27)$$

Transforming the last term with the aid of (3.26), we find that the difference between S and the entropy $S_0 = V_0 N \ln (pe/N)$ of the uniform distribution of the impurities is

$$S - S_0 = \int_V \left[(N+f) \ln \frac{N}{N+f} + f \right] d^3r. \quad (3.28)$$

If $f(\mathbf{r})$ decreases rapidly enough for the integral (3.28) to converge, the integration can be extended to infinity. Then the probability that a fluctuation $f(\mathbf{r})$ has been produced in a certain part of the volume is $\exp(-\Omega\{f\})$, where

$$\Omega\{f\} = - \int \left[(N+f) \ln \frac{N}{N+f} + f \right] d^3r. \quad (3.29)$$

We introduce now the functionals $V_r\{f\}$ and $\lambda_0\{f\}$, the first being the test-electron potential energy produced by the fluctuation f at the point \mathbf{r} , and the second the electron ground-state energy determined from the Schrödinger equation

$$-\frac{\hbar^2}{2m} \Delta \psi + V_r\{f\} \psi = \lambda_0 \psi. \quad (3.30)$$

In the Debye-screening approximation we have

$$V_r\{f\} = \int f(\mathbf{r}') \varphi(\mathbf{r} - \mathbf{r}') d^3r', \quad (3.31)$$

$$\varphi(\mathbf{r}) = - (e^2/\kappa r) e^{-r/r_D}.$$

The optimal fluctuation $\tilde{f}(\mathbf{r})$ should minimize $\Omega\{f\}$ under the condition

$$\lambda_0\{f\} = -e. \quad (3.32)$$

The corresponding equation is

$$\delta(\Omega\{f\} + \beta \lambda_0\{f\}) = 0, \quad (3.33)$$

where β is a Lagrange multiplier that must be determined from (3.32).

Varying (3.29) and recognizing that

$$\delta \lambda_0\{f\} = \int |\psi(\mathbf{r}')|^2 d^3r' \int \varphi(\mathbf{r}' - \mathbf{r}) \delta f(\mathbf{r}') d^3r', \quad (3.34)$$

we ultimately obtain the expression^[18]

$$\ln \frac{N+\tilde{f}}{N} + \beta \int |\psi(r')|^2 \varphi(r-r') d^3r' = 0, \quad (3.35)$$

which together with (3.30) determines the optimal fluctuation \tilde{f} . The principal term of the logarithm of the state density is given by

$$\ln \frac{\rho(r)}{\rho(0)} = -\Omega(\tilde{f}), \quad (3.36)$$

We now present a rigorous derivation of (3.12) and (3.18) and determine the numerical factors that depend on the form of the fluctuation.

2) Derivation of formula (3.12). The optimal fluctuation corresponding to (3.12) is described by Gaussian statistics. In this case ($f \ll N$), Eq. (3.29) takes the form

$$\Omega(\tilde{f}) = (1/2N) \int \tilde{f}^2 d^3r, \quad (3.37)$$

and in place of (3.35) we obtain

$$\tilde{f} = -N\beta \int |\psi(r')|^2 \varphi(r-r') d^3r'. \quad (3.38)$$

Let us assume that the characteristic dimension of the wave function is $\lambda \ll r_S$. Then

$$\tilde{f} = -N\beta\varphi(r) \quad (r \gg \lambda), \quad (3.39)$$

and the potential energy of the optimal well is, in accordance with (3.31),

$$V_r(\tilde{f}) = -N\beta \int \varphi(r') \varphi(r-r') d^3r' \quad (3.40)$$

or

$$V_r(\tilde{f}) = -\frac{e^4 N \beta r_s}{\kappa^2} \cdot 2\pi e^{-r/r_s}. \quad (3.41)$$

The potential energy drops off over a distance on the order of r_S , and at $\epsilon \gg E_S = \hbar^2/mr_S^2$ the energy of the ground state is close to the bottom of the well. We can therefore determine β from the condition

$$V_r(\tilde{f})|_{r=0} = -\epsilon. \quad (3.42)$$

Then

$$\beta = \frac{\epsilon \kappa^2}{2\pi e^4 N r_s}. \quad (3.43)$$

Substituting (3.43), (3.39), and (3.37) in (3.36), we obtain formula (3.12), and the numerical coefficient in γ turns out to be the same as in (2.13).

We now obtain the wavelength λ of the electron in the ground state. To this end we note that according to (3.38) we have at $r \ll \lambda$

$$\tilde{f} \approx N\beta e^2/\kappa\lambda \quad (3.44)$$

and that \tilde{f} does not depend on r . Thus, the internal part of the fluctuation ($r < \lambda$) is a uniformly charged sphere. For this solution to be self-consistent, the radius of the sphere should be such that the potential produced by the sphere contain an electron level with wavelength on the order of the sphere radius. A sphere of radius λ and charge density (3.44) produces a potential well of depth $N\beta(e^2/\kappa)\lambda$. The radius λ can be obtained by equating this quantity to $\hbar^2/m\lambda^2$. As a result we obtain

$$\lambda \approx r_s (E_0/\epsilon)^{1/2}. \quad (3.45)$$

At $\epsilon \gg E_S$ the inequality $\lambda \ll r_S$ assumed in the derivation is satisfied.

Halperin and Lax^[15] solved Eqs. (3.30) and (3.38) numerically. It is of interest to compare the foregoing analytic solution with the results of these calculations.

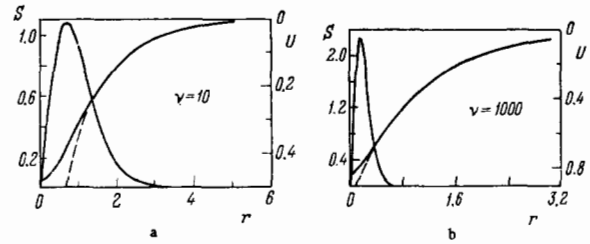


FIG. 4. Plots of the dimensionless potential $U(r)$ and of the wave function $S(r)$ against r/r_S , obtained in [15] with a computer. The dashed line shows the potential calculated from formula (3.41) in the region where it differs from $V(r)$; a) $\nu = 10$; b) $\nu = 10^3$; $\nu = \epsilon/E_S$.

Figure 4 shows the optimal potential and the wave function obtained in^[15] with a computer at $\nu = \epsilon/E_S \gg 1$.

The plots represent the dimensionless potential $U(r) = V_r \kappa^2 / 2\pi e^4 N \beta r_S$ and the dimensionless wave function $S(r) = \sqrt{4\pi} \psi(r) r r_S^{1/2}$. In accordance with (3.41), in those places where $S(r)$ is small $V(r)$ coincides exactly with the plot of the function $\exp(-r/r_S)$, which is shown dashed in Fig. 4. Since we did not obtain the exact form of the wave function, we can only compare (3.45) with Fig. 4 approximately. To this end we assume that the wavelength λ is proportional to the coordinate of the maximum of $S(r)$. The ratio of the wavelengths obtained in this manner at $\nu = 10$ and $\nu = 10^3$ is $\lambda_{10}/\lambda_{1000} = 4.4$. According to (3.45), this ratio is equal to $(100)^{1/3} = 4.6$. Thus, the analytic and numerical solutions are in splendid agreement.

3) Asymptotic density of states in the absence of impurity correlation. We rewrite (3.35) in the form

$$\tilde{f} = N(e^{\chi(r)} - 1), \quad (3.46)$$

where

$$\chi(r) = (\beta e^2/\kappa) \int |\psi(r')|^2 e^{r-r'} r'^2 d^3r'. \quad (3.47)$$

We shall show now that at high energies there exists a spherically-symmetrical solution of (3.30) and (3.46). This solution has the property that the function \tilde{f} decreases exponentially over a distance x that is small in comparison with the wavelength λ of the electron in the ground state (x is of the same order as r_{\max} (3.17)). In addition, it turns out that $\lambda \ll r_S$. Assuming all this beforehand, we should regard the fluctuation as constituting an almost pointlike nucleus of an ion with a charge

$$Z = \int \tilde{f}(r) d^3r, \quad (3.48)$$

and the wave function of the ground state is given by

$$\psi(r) = \frac{1}{\sqrt{\pi} \lambda^{3/2}} e^{-r/\lambda}, \quad (3.49)$$

with $\lambda = a/Z$. Since the ground state should have an energy ϵ , we have

$$Z = (\epsilon/E_0)^{1/2}, \quad \lambda = a (E_0/\epsilon)^{1/2}. \quad (3.50)$$

We shall prove that this solution satisfies the equations. To this end, we substitute (3.49) in (3.47) and obtain the explicit form of $\chi(r)$ and $\tilde{f}(r)$. To determine β , we substitute \tilde{f} in (3.48) and use (3.50).

Substituting (3.49) in (3.47) and expanding in powers of r/λ , we obtain

$$\chi(r) = t - (r^2/x^2), \quad (3.51)$$

where

$$t = \frac{\beta e^2}{\kappa \lambda}, \quad x^2 = \frac{3}{2} \frac{\lambda^2}{t}. \quad (3.52)$$

We see that the assumption made above, namely that $\tilde{f}(r)$ falls off sharply at small distances, is equivalent to the assumption $t \gg 1$. If indeed $t \gg 1$, then at $r < \lambda$ the argument of the exponential in (3.46) is large and

$$\tilde{f}(r) = Ne^{\epsilon} e^{-r^2/\lambda^2}. \quad (3.53)$$

Substituting (3.53) and (3.50) in (3.48), we obtain a transcendental equation for the determination of t :

$$t = \ln \left[\left(\frac{\epsilon}{E_0} \right)^2 \frac{t^{3/2}}{Na^3} \left(\frac{2}{3\pi} \right)^{3/2} \right]. \quad (3.54)$$

From this we get at sufficiently high energy

$$t \approx \ln [(e/E_0)^2 / Na^3] \gg 1, \quad (3.55)$$

and this justifies the assumption made. Thus, the predicted solution does indeed exist.

To calculate $\Omega\{\tilde{f}\}$, we recognize that $\tilde{f} \gg N$ and that (3.29) can be rewritten in the form

$$\Omega\{\tilde{f}\} = \int \tilde{f} \ln(\tilde{f}/Ne) d^3r. \quad (3.56)$$

Substituting (3.53) in (3.56), we easily obtain

$$\Omega\{\tilde{f}\} = Z(t-1) - (3/2)Z. \quad (3.57)$$

This expression contains terms of order Zt and Z . It is therefore impossible to substitute here $Z = \sqrt{\epsilon/E_0}$, and it is necessary to take into account the corrections of order t^{-1} to this expression. The ground-state energy, with the correction for the non-pointlike character of the nucleus, is^[22]

$$e = Z^2 E_0 \left(1 - \frac{4}{3} \frac{(r^2)}{\lambda^2} \right). \quad (3.58)$$

Hence

$$Z = \sqrt{\frac{\epsilon}{E_0}} \left(1 + \frac{2}{3} \frac{(r^2)}{\lambda^2} \right); \quad (3.59)$$

here

$$\langle r^2 \rangle = \frac{1}{Z} \int \tilde{f}(r) r^2 d^3r. \quad (3.60)$$

Substituting (3.53) in (3.60) and (3.59) we obtain

$$Z = \sqrt{\frac{\epsilon}{E_0}} \left(1 + \frac{3}{2t} \right). \quad (3.61)$$

The corrections to Eq. (3.54), obtained with the aid of (3.59), are of the order of t^{-1} , and can be disregarded. Substituting (3.61) in (3.57), we obtain

$$\Omega\{\tilde{f}\} = (e/E_0)^{1/2} (t-1). \quad (3.62)$$

Substitution of (3.62) in (3.63) leads to the result (3.18)^[20], with

$$D(e) = (2/3\pi)^{3/2} t^{3/2} e^{-1}, \quad (3.63)$$

and t is determined by (3.54).

We note, however, that the exponential decrease of $\tilde{f}(r)$, described by (3.53), takes place only if $r < \lambda$. At large distances, it turns out to be smoother. At $r \gg \lambda$ we obtain from (3.47)

$$\chi(r) = \frac{\beta e^2}{\kappa r} e^{-r/r_0}. \quad (3.64)$$

Substituting $\beta e^2/\kappa$ from (3.52), we verify that $\chi(r) \ll 1$ at $r \gg \lambda$, and consequently

$$\tilde{f}(r) = t(\lambda/r) e^{-r/r_0} \quad (r \gg \lambda). \quad (3.65)$$

The potential produced by this part of the charge at the center of the fluctuation leads to a classical level shift by an amount

$$\frac{e^2}{\kappa} \int \frac{f(r')}{r'} d^3r' \approx \frac{e^2}{\kappa} t N \lambda r_0. \quad (3.66)$$

(The shift can be regarded as classical, since the main contribution to the integral is made by the region where $r \approx r_0 \gg \lambda$.) The theory developed above is valid if the right-hand side of (3.66) is small in comparison with ϵ . This calls for the condition $\epsilon > E_1$, where E_1 is determined by (3.20). In addition, of course, we need also the condition $\lambda < r_0$, i.e., $\epsilon > E_S$. These two conditions suffice also to make the expression under the logarithm sign large.

Thus, the region of applicability of formula (3.18) was obtained correctly in the preceding section.

d) **Spectrum of minority carriers.** As will be shown in the next chapter, in a degenerate semiconductor the frequency dependence of the coefficient of the interband absorption of light at frequencies below threshold is determined just by the minority-carrier spectrum. The problem of calculating the density of states has in this case two important features:

a) The majority impurities are repulsion centers for the minority carriers (for example, a charged donor for a hole).

b) The electron and hole masses usually are greatly different from each other. The problem has therefore many aspects. As we have seen in the derivation of (3.12), an important role was played by the condition $\gamma > E_S = \hbar^2/mr_S^2$, meaning that a typical potential well with dimension r_S contains quantum levels. If we are dealing with minority carriers, then it is necessary to substitute their mass in the expression for E_S , and the mass of the majority carriers that produce the screening in the expression for r_S . This can give rise to different situations, which we shall now analyze.

1) **The classical case ($\gamma > E_S$).** We consider the hole spectrum in an n-type semiconductor, assuming that the hole mass m_h is larger than the electron mass m . We assume first that there is no compensation at all, i.e., there are only donor impurities, and the strong-doping condition $Na^3 \gg 1$, where $a = \hbar^2/m_e^2$ is the Bohr radius of the electron, is satisfied for the electrons. The condition $\gamma > E_S$ is not easier to satisfy, since it takes the form $\hbar^2/m_h r_S^2 < \gamma$ or $(m_h/m)(Nr_S^3)^{1/6} > 1$.

Since the donors repel the holes, deep hole states are produced not by clusters but by donor voids. In Gaussian statistics, the clusters and the voids are equally probable. It is therefore easy to verify that the conclusion that leads to formula (3.12) remains unchanged. According to (2.15), Gaussian statistics are applicable at $\epsilon \ll \Gamma$. If the clusters are large, their symmetry or that of the voids is violated. It is obvious that the spectrum of the single-electron problem has an end point at $\epsilon = \Gamma$. Indeed, if the donors free completely a region with linear dimension $R \gg r_S$, then all that remains in the center of this region is the potential produced by the positive background, and this potential raises the energy of the hole by an amount Γ . It is impossible to produce a larger increase.

Near the end point, the single-electron approximation is valid only if the Fermi energy $\mu \gg \Gamma$. This takes place if the number of electrons is much larger than that of the donors (for example, if the electrons are produced by additional illumination). If $n = N$, then μ and Γ are equal apart from numerical coefficients. Therefore the single-electron approximation is not valid near the end point. In regions with decreased donor concentration, the electron density is likewise

reduced. This increases the screening radius, and consequently also the dimension of the region that must be rid of donors in order to obtain the required rise of the bottom of the conduction band and of the top of the valence band (Fig. 5). Near the end point, the screening radius tends to infinity and therefore the density of states vanishes exponentially.

Let us find the form of the density of states of the holes near the end point^[13]. We assume that the fluctuation has produced a region with a donor density $\tilde{N} \ll N$. The energy scheme of the contact with such a region is shown in Fig. 5. The contact potential difference that raises the bottom of the conduction band and the top of the valence band by an amount ϵ is given by the relation $\mu - \epsilon \approx \hbar^2 \tilde{N}^{2/3} / m$. This rise does indeed occur if the dimension of the region in which the fluctuation takes place exceeds the screening radius $\tilde{r}_S = r_S (\tilde{N}/N)^{1/6}$ in this region. The probability of this fluctuation is $\exp(-N\tilde{r}_S^3)$. Expressing \tilde{r}_S in terms of $(\mu - \epsilon)$, we obtain for the hole density of states

$$\ln \frac{\rho(\epsilon)}{\rho(0)} \approx -N r_S^3 \left(\frac{\mu}{\mu - \epsilon} \right)^{3/4}. \quad (3.67)$$

(When investigating $\rho(\epsilon)$ for holes, we reckon ϵ upward from the top of the valence band. The chemical potential μ in (3.67) is reckoned, of course, from the bottom of the conduction band.) If μ and ϵ are of the same order and $\mu - \epsilon$ is of the order of μ , then the result (3.67) coincides with (3.12), as expected. We note, however, that in the derivation of (3.67) we have assumed that the electron gas in the fluctuation is ideal. This calls for satisfaction of the condition $Na^3 \gg 1$ or $\mu - \epsilon \gg E_0$. (All these formulas, of course, contain the electron effective mass.) Since $E_0 \ll \mu$, formula (3.67) describes the decrease of $\rho(\epsilon)$ in a rather wide interval.

If it is assumed that the semiconductor contains compensating acceptors, then the state density at an arbitrary depth differs from zero. At a sufficiently large ϵ it is possible to use formula (3.18), in which N , a , and E_0 should be replaced by $a_h = \hbar^2 \kappa / m_h e^2$ and $E_h = \hbar^2 / 2 m_h a_h^2$. (For details see^[13,19].)

2) **Quantum case** ($\gamma < E_S$). In typical semiconductors, the heavy-hole mass is much larger than the electron mass. Therefore the quantum-case condition $\gamma < E_S$ is easily realized if the electron spectrum is investigated in a p-type semiconductor. We assume as before that the strong-doping condition $Na a_h^3 \gg 1$ is satisfied for the majority carriers. Since this is equivalent to the condition $Na r_S^3 \gg 1$, it follows from the inequality $\gamma < E_S$ that $r_S \ll a$, where a is the Bohr radius of the electron. (We recall that the screening is determined by the holes, and that $E_S = \hbar^2 / m r_S^2$, with m the effective mass of the electron.) This means that an individual donor impurity has no bound state.

As in the classical case, an important role is played at low energies by fluctuations to which Gaussian statistics are applicable ($|Z| \ll Na r_S^3$). We can therefore use formulas (3.6) and (3.7), bearing in mind that we are dealing with acceptor voids that produce potential wells for electrons. As already mentioned, a plot of the function $\ln W(R, \epsilon)$ coincides with the curves of Fig. 2 at $R > r_q = \hbar / \sqrt{m\epsilon}$. Let at first $\epsilon < E_S$, i.e., $r_q > r_S$. Then (Fig. 6) at $R > r_q$ the function $\ln W(R, \epsilon)$ decreases with R . The fluctuations having a radius R satisfying the condition $r_S \ll R \ll \hbar / \sqrt{m\epsilon}$ can produce a level ϵ only if the well depth is $V \approx \hbar^2 / m R^2 \gg \epsilon$

FIG. 5. Bending of the bands in a region depleted of donors. The occupied states of the conduction band are shown shaded.

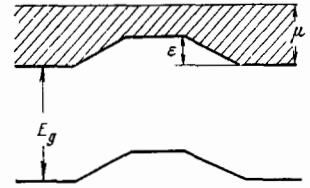
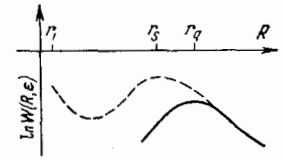


FIG. 6. Solid curve—the same as in Fig. 3 but for $\epsilon < E_S$, dashed— $\ln W(R, V)$.



(narrow well with shallow level). Substituting (3.7) in this condition and expressing Z in terms of R , we obtain

$$Z = a R / r_S^2, \quad (3.68)$$

$$\ln W(R, \epsilon) = -\frac{Z^2}{N_A R^3} = -\frac{a^2}{N_A R r_S^4}. \quad (3.69)$$

From this we see that at $R < \hbar / \sqrt{m\epsilon}$ the function $\ln W(R, \epsilon)$ decreases with decreasing R (Fig. 6). It is easy to show that it continues to decrease also at $R < r_S$. Thus, the optimal fluctuation is possessed by a radius $R = \hbar / \sqrt{m\epsilon}$. Substituting this radius in (3.69), we obtain^[15-19]

$$\ln \frac{\rho(\epsilon)}{\rho(0)} = -\left(\frac{\epsilon}{E_0} \right)^{1/2} \frac{E_0}{\Gamma} \quad (\epsilon < E_S). \quad (3.70)$$

Thus, unlike in the classical case, where the exponential decrease of $\rho(\epsilon)$ begins at $\epsilon = \gamma$ and is described by (3.12), in the quantum case the decrease begins at $\epsilon = E_0 (\Gamma / E_S)^2$ and is described by (3.70).

The subsequent course of $\rho(\epsilon)$ depends on the ratio of E_S and Γ . If $E_S < \Gamma$, then at $\epsilon = E_S$ the lengths r_q and r_S become comparable, (3.70) goes over into (3.12), and the subsequent course of $\rho(\epsilon)$ is the same as in the classical case. On the other hand, if $E_S > \Gamma$, then the Gaussian statistics are violated at $r_q > r_S$ and (3.12) does not hold at all. If there are no attracting centers, the electron spectrum terminates at $\epsilon \approx \Gamma$. In the presence of compensation, the density of states differs from zero also at high energies, and is determined by the donor fluctuations. The asymptotic form in terms of energy is described as before by formula (3.18)^[1].

e) **Asymptotic form of the state density with allowance for correlation and distribution of the impurities.** In the preceding arguments it was assumed that there was no correlation in the distribution of the charge centers. If the centers are produced by irradiation at low temperatures, this assumption may be correct. On the other hand, if the sample has been subjected to high-temperature treatment during the course of which the impurities could move freely, then an interaction-induced correlation appears in their distribution. The impurity diffusion coefficient decreases very sharply with temperature. Since the samples cool sufficiently rapidly, it can be assumed that the impurity distribution is a "snapshot" of the plasma existing at a certain temperature T_0 corresponding to the cessation of the diffusion^[23]. This temperature is usually close to the melting temperature.

Allowance for the correlation turns out to be important in the calculation of the asymptotic form of $\rho(\epsilon)$ at large ϵ . Indeed, we have assumed that the probability

of formation of a nucleus consisting of Z impurities having a radius R is $\exp[-Z \ln(Z/NR^3)]$. At the temperature T_0 , however, these impurities repel one another. To gather them together it is necessary to perform work equal to $Z^2 e^2 / \kappa R$. Therefore the probability of such a fluctuation is

$$\exp\left(-Z \ln \frac{Z}{NR^3}\right) \exp\left(-\frac{Z^2 e^2}{\kappa R T_0}\right). \quad (3.71)$$

At sufficiently large Z , the second factor must become more important than the first. Let us find the dimension of the optimal fluctuation in this case. If $R > \hbar/\sqrt{m\epsilon}$, then the well is classical and $\epsilon \approx Ze^2/\kappa R$. (We have in mind values of R that are small in comparison with the screening radius.) Hence $Z \approx \kappa R \epsilon / e^2$, and the probability $\exp(-\kappa R \epsilon^2 / e^2 T_0)$ of such a well decreases with increasing R . If $R < \hbar/\sqrt{m\epsilon}$, the well represents a pointlike nucleus, $Z = \sqrt{\epsilon/E_0}$, and the probability is equal to $\exp(-\epsilon^2/E_0 \kappa R T_0)$ and decreases with decreasing R . Thus, the optimal fluctuation has a dimension $R \approx \hbar/\sqrt{m\epsilon}$ of the order of the radius of the first orbit. Nonetheless, $Z \approx \sqrt{\epsilon/E_0}$. Substituting these values of R and Z in the second factor, we obtain^[20,24]

$$\ln \frac{\rho(z)}{\rho(0)} = -C \frac{e^{3/2}}{E_0^{1/2} T_0}, \quad (3.72)$$

where C is a numerical coefficient. This is the asymptotic form of the state density with allowance for the impurity correlation. In^[20] we obtained a dimensionless equation that determines the form of the optimal fluctuation and the value of C . Formula (3.18) is replaced by (3.72) at $\epsilon > T_0 \ln[(T_0/E_0)^2 D(T_0)/Na^3]$.

4. INTERBAND ABSORPTION OF LIGHT

a) Connection between the interband light absorption coefficient (ILAC) and the density of states. The most important method of investigating fluctuations of levels are experiments on interband absorption of light near the threshold. Typical experimental data obtained with n-GaAs are shown in Fig. 7. We see that the ILAC decreases by four orders of magnitude when the quantum energy decreases by an amount that is negligible in comparison with the width of the forbidden band ($E_g = 1.51$ eV at $T = 77^\circ\text{K}$). With increasing electron density, the curves shift towards the short-wave region and become more gently sloping. The shift of the curves is connected with the filling of the conduction band (the Moss-Burstein effect). In strongly doped n-type semiconductors (SDS) the transition at low temperatures is to the Fermi level (Fig. 8), since all the states below it are filled. The threshold energy exceeds the width E_g of the forbidden band in this case by an amount equal to the Fermi energy μ , if account is taken of transitions from the bottom of the valence band, accompanied by change of momentum (indirect transitions), or else by an amount $\mu[1 + (m/m_h)]$, if only direct transitions are taken into account (see Fig. 8). The indirect transitions become possible because of the presence of impurities and, as a rule, their probability in SDS differs little from the probability of the direct transitions. We shall therefore henceforth take the threshold energy to be the minimal energy of the indirect transitions.

At a finite temperature, the ILAC can be different from zero at frequencies below the threshold frequency, owing to the holes in the Fermi occupancy. Since the probability of the existence of a hole with an energy lower than μ by an amount ϵ is proportional to $\exp(-\epsilon/T)$, the ILAC decreases with frequency ω like $\exp[(\mu + E_g - \hbar\omega)/T]^2$.

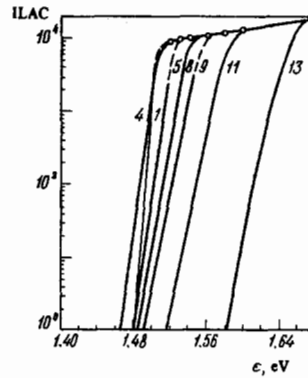


FIG. 7

FIG. 7. ILAC (in cm^{-1}) as a function of the quantum energy (in eV) in n-GaAs samples with electron densities (cm^{-3}): 2×10^{16} (1); 2.2×10^{17} (4); 5.3×10^{17} (5); 1.2×10^{18} (11); and 6.5×10^{18} (13) (according to the data of [40]; $T = 77^\circ\text{K}$).

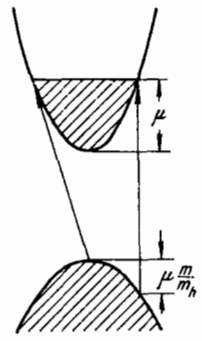


FIG. 8

FIG. 8. Transitions with threshold quantum energy. Vertical arrow—direct transition, inclined arrow—indirect transition.

With decreasing temperature, this absorption mechanism turns out to have low probability³⁾. The only absorption mechanism that exists at zero temperature consists of transitions from fluctuation levels that lie above the top of the valence band. For the sake of argument, we shall again speak of an n-type semiconductor.

When a light quantum with energy $\hbar\omega < E_g + \mu$ is absorbed, a hole is produced and should be located above the top of the unperturbed valence band, by an amount not less than $\epsilon_h = E_g + \mu - \hbar\omega$. The scheme of such transitions, in the presence of a fluctuation potential that bends the boundaries of both bands is shown in Fig. 9. The number of fluctuation levels of the holes decreases exponentially with increasing ϵ_h . As a result, the ILAC decreases exponentially with decreasing frequency.

However, the ILAC is proportional not only to the probability of the existence of a deep hole level, but also to the probability of the interband transition. The latter can also be exponentially small, since the hole level is produced by a cluster of negatively charged acceptors, and the wave function of the electron can be greatly impoverished in this region. As shown in Chap. 3, in the region of Gaussian fluctuations the potential does not distort strongly the electronic states near the Fermi level (we have used this fact when we assumed a Debye screening). In this case the probability of the transition to the Fermi level is not low and the argument of the exponential in the ILAC is obtained from the argument of the exponential of the hole state density by replacing ϵ by $\epsilon_h = E_g + \mu - \hbar\omega$ ^[25].

In the region of non-Gaussian fluctuations, the principal role in the hole state density is played by clusters of acceptors that form nuclei of multiply charged ions, the ground state of which has an energy ϵ . At $\epsilon > \mu$, the impoverishment of the wave function of an electron with energy μ can be appreciable. This impoverishment, however, occurs in a relatively small region of space, and it may turn out^[20] that it does not affect the frequency dependence of the ILAC.

Thus, in a strongly doped and weakly compensated semiconductor with degenerate carriers, the frequency dependence of the ILAC duplicates the density of states

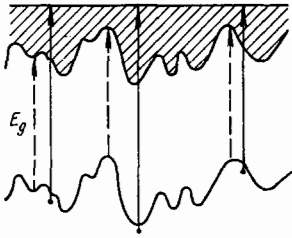


FIG. 9. Scheme of interband transitions in a degenerate semiconductor at $T = 0$. The sinuous lines are the band boundaries bent by the fluctuation potential. The occupied states of the conduction band are shaded.

of the minority carriers (for example, holes in the n -type semiconductor case considered above).

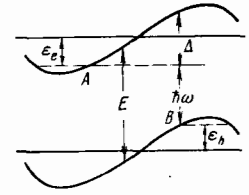
b) Absorption of light as a result of Gaussian fluctuations in the absence of carrier degeneracy. We consider a strongly doped semiconductor in which the Fermi level lies deep in the forbidden band. This can be the result of a high temperature or strong compensation. This includes also the situation (which exists, for example, in germanium), when quantum absorption gives rise to the transition of an electron to an unfilled band located over the valence band, and the electrons form a Fermi-occupancy in the lateral extremum, while the Fermi level passes much lower than the bottom of the unfilled band into which the electron goes over. Let, furthermore, the sample contain charged donors and acceptor with total density $N_t = N + N_A$. We shall assume them to have a Coulomb potential up to a certain distance r_0 , after which the potential drops off rapidly. This decrease can be due either to electron screening or to correlation in the disposition of the impurities. What will be important to us is only the fact that the impurity correlation can be disregarded in Gaussian fluctuations of dimension $R \ll r_0$ and that the length r_0 is large, so that the fluctuation potential can be regarded, in accordance with the terminology of Chap. 3, as classical for both electrons and holes, i.e.,

$$\frac{\hbar^2}{mr_0^2} \ll \gamma, \quad \frac{\hbar^2}{m_h r_0^2} \ll \gamma, \quad \gamma = \frac{e^2}{\kappa r_0} (N_t r_0^3)^{1/2}. \quad (4.1)$$

As already shown, in this case the state density of the electrons or holes drops off in the interior of the forbidden band in accordance with (3.12), and the optimal fluctuations are wells having a dimension r_0 and having many levels. It is easy to understand that in this case the absorption coefficient is not a replica of the state density. This is clearly seen in Fig. 10. Let us assume that we are investigating a transition that has caused the production of an electron and a hole with energies ϵ_e and ϵ_h (these energies are reckoned upward from the bottom of the conduction band and from the top of the valence band). This is accompanied by absorption of a quantum with a deficit $\Delta = \epsilon_h - \epsilon_e$. (The quantum deficit Δ is defined as the amount by which the energy of this quantum is less than the width of the forbidden band, i.e., $\Delta = E_g - \hbar\omega$.)

As seen from Fig. 10, if $\Delta > 0$, then the regions in which the electron and hole are located are separated in space. Indeed, the region to the right of the point A is classically inaccessible to the electron, and the region to the left of the point B is classically inaccessible to the hole. The absorption coefficient contains the overlap integral of the wave functions of the electron and hole. We let the electron mass and the hole mass go to infinity (at fixed r_0). Then the tunneling probability vanishes and the absorption of a quantum with $\Delta > 0$ becomes impossible. At the same time, the state density determined only by the probability of producing the potential well is expressed by the classical

FIG. 10. Absorption of a quantum with a deficit Δ in a nondegenerate semiconductor. Solid horizontal lines—boundaries of unperturbed bands, bent lines—boundaries of bands bent by the impurity potential (E_g is designated E).



formula (3.12), which does not contain the mass at all. Thus, the absorption of light in this case calls for a special analysis. In essence, this is the Franz-Keldysh effect but not in an external electric field, but in a random field of charged impurities.

We solve this problem by the optimal-fluctuation method^[26], i.e., we obtain the impurity configuration that makes the maximum contribution to the absorption of light with a specified deficit. In the region of large deficits, where the absorption coefficient $K(\Delta)$ is exponentially small, the maximum corresponding to the optimal fluctuation turns out to be very sharp. Therefore the principal term $\ln K(\Delta)$ is determined by the contribution of the optimal fluctuation. Of course, this method does not make it possible to determine the pre-exponential term in $K(\Delta)$.

We present only a simplified derivation analogous to the uniformly charged sphere approximation (Chap. 3), which enables us to determine the argument of the exponential in $K(\Delta)$ accurate to a numerical factor. This factor is determined in the rigorous theory constructed in^[26].

Let us assume that fluctuation of the impurity density in a volume with linear dimension R has produced a homogeneous electric field \mathcal{E} . We assume that R and \mathcal{E} are connected by the relation $e \mathcal{E} R = \Delta$. This is necessary to enable a quantum with a deficit Δ to be absorbed in the field of such a fluctuation. (The absorption of a quantum occurs also at $R > \Delta/e\mathcal{E}$, but such a fluctuation has obviously a low probability). The excess number of impurities necessary to produce the required fluctuations is determined from the condition $\mathcal{E} = Z\epsilon/\kappa R^2$, i.e.,

$$Z = \mathcal{E} \kappa R^2/e = \kappa R \Delta/e^2.$$

(We do not write out here the numerical factors that depend on the form of the fluctuation). The contribution made to the absorption coefficient by such a fluctuation is proportional to the quantity

$$\exp\left(-\frac{Z^2}{N_t R^3}\right) \exp\left(-\frac{R \sqrt{m\Delta}}{\hbar}\right). \quad (4.2)$$

The first factor is the probability of the appearance of Z excess impurities in the volume R^3 . The second factor is the probability of tunneling of the electron to a depth R (we assume for simplicity that the hole mass is larger than the electron mass and that the hole does not tunnel). Expressing Z in terms of R and Δ , we rewrite (4.2) in the form

$$\exp\left(-\frac{\kappa^2 \Delta^2}{e^4 N_t R} - \frac{R \sqrt{m\Delta}}{\hbar}\right), \quad (4.3)$$

from which it is clear that at a given Δ the tunneling probability increases with decreasing R , whereas the probability of fluctuation production decreases.

Let us find the dimension of the optimal fluctuation R from the condition of the maximum of the argument of the exponential in (4.3):

$$\tilde{R} = a \left(\frac{\Delta}{E_0} \right)^{3/4} \frac{1}{(N_1 a^3)^{1/2}}. \quad (4.4)$$

Substituting (4.4) in (4.3), we obtain the contribution made to $K(\Delta)$ from the optimal fluctuations. In accordance with the foregoing, we obtain ultimately

$$\ln \left[\frac{K(\Delta)}{K(0)} \right] = -\beta \left(\frac{\Delta}{E_0} \right)^{5/4} \frac{1}{(N_1 a^3)^{1/2}}. \quad (4.5)$$

Here β is a numerical factor that cannot be obtained from such a simplified derivation. In^[28] it is shown that if $m_h \gg m$, then $\beta = 2/5 \sqrt{\pi}$. Later on Merkulov and Perel'^[37] have shown that at comparable electron and hole masses it is necessary to use in (4.5) the reduced mass $mm_h/(m+m_h)$, and the coefficient β remains unchanged. It is seen from (4.5) that the law governing the decrease of the absorption coefficient differs significantly from the law (3.12) governing the decrease of the state density.

We now investigate the region of applicability of (4.5). It is very important in the foregoing derivation that the potential of the impurities was of the Coulomb type, at least at a distance on the order of \tilde{R} . Therefore the result is valid provided only $\tilde{R} < r_0$ or, taking (4.4) into account,

$$\Delta < \Delta_1, \quad \Delta_1 = E_0 (r_0/a)^{4/3} (N_1 a^3)^{2/3}. \quad (4.6)$$

On the other hand, in order for (4.5) to be applicable we need to satisfy the condition $|\ln[K(\Delta)/K(0)]| \gg 1$, or

$$\Delta \gg \Delta_2, \quad \Delta_2 = E_0 (N_1 a^3)^{2/5}.$$

From the first inequality of (4.1) it follows that $\Delta_1 > \Delta_2$, i.e., the region of applicability of (4.5) exists and is wider the larger r_0 .

The fluctuation considered by us, as seen from Fig. 10, represents a potential well for an electron and an adjacent potential well for a hole. In our derivation it was also assumed that the electron energy has been lowered by an amount Δ , and the hole energy has been raised the same amount, i.e., each potential well has a level with an energy on the order of its depth. To this end it suffices to satisfy the inequality $\hbar^2/m\tilde{R}^2 \ll \Delta$, which follows from (4.7) and imposes no additional limitations.

Let us see now what happens at $\Delta > \Delta_1$. If $\tilde{R} > r_0$, then at $R = r_0$ the second term in (4.3) is small in comparison with the first, i.e., the tunneling is negligible. As we have seen in Sec. (b) of Chap. 3, the probability of producing a potential well of depth Δ and dimension r decreases at $R > r_0$ with increasing R (the potential of the more remote impurities does not extend to the center). Therefore just as in the theory of the density of states, the dimension of the optimal cluster is in this case r_0 . Substituting in (4.3) $R = r_0$, we obtain at $\Delta > \Delta_1$

$$\ln \frac{K(\Delta)}{K(0)} = -\frac{\Delta^2}{\gamma^2}, \quad (4.8)$$

which is the same expression as for the density of states.

It is possible that even at $\Delta < \Delta_1$ the non-Gaussian fluctuations of atomic type will make a larger contribution to the ILAC than the Gaussian fluctuations considered above. In this case there is no region at all in which (4.8) is valid.

The question of light absorption in compensated semiconductors has been the subject of many papers, in which various methods were used. We shall attempt to

compare the results. We discuss first the work of Redfield et al.^[27-30]. The idea of their papers is that the ILAC with a deficit Δ in a homogeneous electric field \mathcal{E} averages out with the distribution function of the electric field $F(\mathcal{E})$ produced by the charged impurities:

$$K(\Delta) = \int K_{\mathcal{G}}(\Delta) F(\mathcal{E}) d\mathcal{E}. \quad (4.9)$$

According to Keldysh^[31] and Franz^[32]

$$K_{\mathcal{G}}(\Delta) \sim \exp\left(-\frac{\sqrt{m\Delta}}{\hbar e} \frac{\Delta}{\mathcal{E}} \eta\right), \quad (4.10)$$

where η is a numerical coefficient.

In^[27,28], a Holtsmark distribution was used for the function $F(\mathcal{E})$. At large \mathcal{E} we have^[33]

$$F(\mathcal{E}) \sim 1/\mathcal{E}^{5/2}. \quad (4.11)$$

Therefore at large Δ in the interval (4.9) an important role is played by $\mathcal{E} \approx \mathcal{E}_C = \sqrt{m\Delta}/\hbar e$ and, in contrast to (4.3), the integral is not exponentially small. The reason for this discrepancy is obvious. Formula (4.10) is valid provided only that the field \mathcal{E} is homogeneous, at least over the distance $\Delta/e\mathcal{E}$ over which the deficit Δ is accumulated (see Fig. 10). On the other hand, the asymptotic form (4.11), corresponds to a field produced by one impurity located at a distance $R(\mathcal{E}) = \sqrt{(e/\kappa)\mathcal{E}}$ away from the observation point. This field can be regarded as homogeneous over a distance $R \ll R(\mathcal{E})$. At $\mathcal{E} = \mathcal{E}_C$ we have $\Delta/e\mathcal{E}_C = R(\mathcal{E}_C) (\Delta/E_0)^{1/4}$. We see therefore that at $\Delta > E_0$ the indicated procedure is contradictory.

In^[30] (see also^[34]) it is noted that in the calculation of $K_{\mathcal{G}}(\Delta)$ it is important to take into account the electron-hole interaction. It is clear that if the quantum deficit is large enough this interaction is negligible and the asymptotic form (4.10) is valid. Numerical calculations performed in^[29] have shown, however, that there exists a rather wide intermediate region of Δ , where

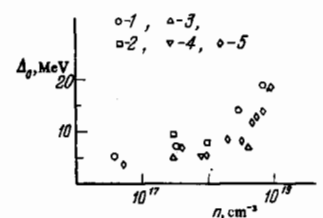
$$K_{\mathcal{G}}(\Delta) \sim \exp(-\Delta/\mathcal{E}C), \quad (4.12)$$

with C independent of \mathcal{E} or Δ . It is proposed in^[30] that $F(\mathcal{E}) \sim \exp(-3\mathcal{E}^2/2\mathcal{E}_{ms}^2)$. Then it follows from (4.9) and (4.12) that $K(\Delta) \sim \exp(-\Delta/C\mathcal{E}_{ms})$. It seems to us, however, that the representation of $F(\mathcal{E})$ by a Gaussian function is not justified, since the mean-squared field \mathcal{E}_{ms}^2 for Coulomb centers diverges at short distances.

As shown by Merkulov and Perel'^[35], allowance for the interaction of the electron and the hole as a small term to the argument of the exponential (4.10) if $\Delta^2 \gg e^3 \mathcal{E}$. Substituting in it the inequality $e\mathcal{E} = \Delta/\tilde{R}$, where \tilde{R} is given by (4.4), it is easy to verify that the electron-hole interaction can actually be disregarded in the derivation of (4.5).

The result of Bonch-Bruевич^[36] likewise differs somewhat from (4.5), but it is difficult to explain the cause of the discrepancy in this case, since the most important formula (12) of that paper is presented with-

FIG. 11. Dependence of Δ_0 on the carrier density in n-gaAs in accordance with the following data: [38] (1), [39a] (2), [39b] (3), [39c] (4) and [40] (5).



out derivation, and there is no physical interpretation of the result.

In conclusion we note an interesting paper by Merkulov and Perel^[37], in which the optimal-fluctuation method described above was used to construct the theory of electroabsorption in SDS.

c) Discussion of Experimental Data

Oh no, what is similar to you is only the ghost which you yourself recognizes, not I.

(Goethe, Faust)

In this section we shall attempt to use the theoretical concept developed above to explain experimental data on interband absorption of light.

In semiconductors, the experimentally observed ILAC at frequencies below the threshold usually agrees well with the formula

$$\ln \frac{K(\omega)}{K(\omega_{\text{thr}})} = -\frac{\hbar(\omega_{\text{thr}} - \omega)}{\Delta_0}, \quad (4.13)$$

where $\hbar\omega_{\text{thr}}$ is the threshold energy and Δ_0 is a characteristic energy that does not depend on the frequency. The first difficulty which we encounter is that neither of the considered cases of absorption as a result of fluctuation levels gave rise to the linear relation $\ln K(\omega) \sim -(\omega_{\text{thr}} - \omega)$. All the obtained rules, however, were asymptotic, and the measurements are always carried out in a rather narrow frequency interval, in which the plots of $\sqrt{\Delta} \ln \Delta$ or $\Delta^{5/4}$ are difficult to distinguish from straight lines.

The most complete experimental data, including measurements at helium temperature, are available for n-type gallium arsenide. We confine ourselves to their analysis. Figure 11, which is borrowed from^[38], shows a plot of Δ_0 and the electron density in GaAs of n-type. The circles denote the results Pankove^[38] obtained at $T = 5^\circ$, and the remaining data were obtained at nitrogen temperatures in^[39, 40]. At $T = 77^\circ$ K, samples with electron densities $n > 10^{17} \text{ cm}^{-3}$ are degenerate. Therefore the absorption coefficient duplicates the density of states of the valence band.

Assume that the samples are not compensated, i.e., that there are only electrons and positively-charged donors. We know that in this case the state density above the unperturbed valence band decreases like $\exp(-\epsilon^2/\gamma^2)$. This holds true if $\epsilon \ll \mu$, where μ is the Fermi energy, while at ϵ close to μ the state density vanishes in accordance with (3.67). The ratio μ/γ is equal to $(Nr_s^3)^{1/2}$, apart from a numerical factor: Therefore the presence of a Gaussian section is most essentially connected with satisfaction of the condition $Nr_s^3 \gg 1$, i.e., with the presence of a gas parameter. In n-GaAs we have $(4\pi/3)Nr_s^3 = (1/2)(N/10^{18})^{1/2}$, from which we see that the gas parameter is practically non-existent at the concentrations investigated in^[39-40]. This means that the Debye theory is not applicable and the radius of action r_s should be regarded as close to the average distance between the electrons. Therefore the long-range action, which is so important for the Gaussian section, does not exist. The energies μ and γ become quantities of the same order when r_s is replaced by $N^{-1/3}$. If we calculate γ by formula (2.13), then we see that $\gamma > \Delta_0$ in the entire region of concentrations represented in Fig. 11. Thus, at $N = 10^{18}$ and 10^{19} cm^{-3} we have $\gamma = 15$ and 47 MeV , respectively. In addition,

it is seen in Fig. 11 that Δ_0 depends on N not in a power-law fashion but logarithmically. All this leads us to a very important conclusion: The donor-density fluctuations cause only a narrowing of the forbidden band, by an amount on the order of γ . On the other hand, the tail of the absorption coefficient must apparently be attributed to fluctuations of minority impurity^[19].

Let us assume that the samples are compensated. Because of the large mass of the heavy hole, the radius of the majority acceptor state is small in comparison with r_s . There exist therefore states on one acceptor. On going deeper into the forbidden band, clusters of 2, 3, etc. acceptors become more important in the state density. At a sufficient depth in the forbidden band, formula (3.18) (with acceptor density and hole mass), which is equivalent to the ILAC, becomes valid^[41].

Comparison of formula (4.18) with experiment is difficult for two reasons. First, the acceptor concentration in the employed samples is unknown. The usual methods that make it possible to assess the degree of compensation (for example, measurement of the mobility) are suitable only when the donor and acceptor densities are close. If the absorption coefficient at large deficits is indeed determined by the acceptors, then it should feel them regardless of the donors also at very low densities. We can therefore calculate only the acceptor density necessary for the formation of the observed tail of the density of states, and to examine the extent to which it is reasonable.

The second reason is that formula (3.18) is an asymptotic expression that is valid when $\epsilon/E_h \gg 1$. In the experiments referred to above, we observed the region $\epsilon/E_h < 5$. This is patently insufficient to regard the charge of the nucleus as a continuous variable (see (Sec. (b) of Chap. 3)). Nonetheless, we can obtain from (3.18) an order-of-magnitude estimate. In the observed region, the dependence of (3.18) on ϵ differs little from linear. To calculate Δ_0 we can use the following formula:

$$\frac{1}{\Delta_0} = -\frac{d \ln K(\Delta)}{d\Delta} = \frac{1}{E_h} \left\{ 1 + \frac{1}{4} \ln \left[\frac{16D(4E_h)}{NAa_h^2} \right] \right\}. \quad (4.14)$$

(We put $\epsilon/E_h = 4$. Since the dependence is close to linear, the derivative depends little on the choice of the point). Calculation by means of formula (4.14) with $a_h = 30 \text{ \AA}$ yields $\Delta_0 = 9.1 \text{ meV}$ at $N_A = 10^{17} \text{ cm}^{-3}$, $\Delta_0 = 12.3 \text{ meV}$ at $N_A = 10^{18} \text{ cm}^{-3}$, and $\Delta_0 = 20.3 \text{ meV}$ at $N_A = 10^{19} \text{ cm}^{-3}$. These results agree with the experimental data shown in Fig. 11, if it is assumed that the acceptor density in the samples increases with increasing donor density and is comparable with it in order of magnitude.

An indication of the role of the acceptors in the formation of the tail of the absorption coefficient is the appreciable spread of the points in Fig. 11. Thus, for two samples with identical electron density, equal to $6.8 \times 10^{18} \text{ cm}^{-3}$, Pankove^[38] and Hill^[40] obtained values of Δ_0 that differed by 30%. It is clear, however, that under equal conditions we have $\Delta_0(5^\circ \text{ K}) \leq \Delta_0(78^\circ \text{ K})$, yet in this case the opposite inequality has been observed. One can therefore assume that the samples used in^[38] were compensated.

From this point of view it is of interest to discuss the results of Hwang^[41]. The experimental curves obtained at 77° K are shown in Fig. 7. The values of Δ_0 obtained by us with the aid of this curve are listed in

N	1	4	5	8	9	11	13
n, cm^{-3}	$2 \cdot 10^{16}$	$2 \cdot 10^{17}$	$5.3 \cdot 10^{17}$	$1.2 \cdot 10^{18}$	$1.6 \cdot 10^{18}$	$3.1 \cdot 10^{18}$	$6.5 \cdot 10^{18}$
Δ_0, MeV	2.6	4.3	4.6	5.7	6.3	6.6	6.6

the table. The numbers of the samples correspond to the numbers in Fig. 7.

Attention is called first of all to the fact that when the doping is increased Δ_0 tends to 6.6 meV and does not depend on the concentration. This value of Δ_0 is undoubtedly of temperature origin, since $T = 6.6 \text{ meV}$ (77°K). From the fact that such a slope is possessed only by sufficiently doped samples, and that the slope is much larger for weakly doped samples, it follows that these are not transitions with phonon absorption, but temperature smearing of the Moss-Burstein threshold. The associated shift of the absorption curve is clearly seen in Fig. 7. We note now that in the case of sample 13, for example, the donor density is not less than $6.5 \times 10^{18} \text{ cm}^{-3}$, and consequently, according to (2.13), γ is not less than 38 meV, which is much larger than T . This confirms the point of view that the donor-density fluctuation does not produce the absorption-coefficient tail in degenerate n-GaAs. It follows also from Hwang's experiment that in his samples 11-13 the characteristic energy of the tail of the valence band was smaller than 6.6 meV, for otherwise the absorption coefficient would reproduce this tail and not the thermal smearing of the Fermi level. On the other hand, in Pankove's experiment at $T = 5^\circ\text{K}$, performed on a sample with approximately the same electron density ($6.8 \times 10^{18} \text{ cm}^{-3}$), a value $\Delta_0 = 19 \text{ meV}$ was observed. This fact can also be explained by assuming that the ILAC tail is formed by acceptors and that the samples of^[38] were more complicated.

Thus, the only possibility of explaining the experimental data in n-GaAs is seen by us in the hypothesis that the ILAC tail is due to acceptors. Unfortunately, the experiments known to us do not offer a decisive proof of this hypothesis. Data pertaining to other semiconductors are much less skimpy, and their analysis yields little information^[13]. The most important problem in this region is, in our opinion, that of experimentally determining the role of the minority impurities in the formation of the ILAC tail. If the hypothesis discussed above is confirmed, new theoretical investigations will be necessary, aimed at numerically calculating the ILAC in the region of not too large quantum deficits.

The author takes the opportunity to thank B. I. Shklovskii for numerous discussions of the questions touched upon here.

¹⁾The transition from (3.70) to (3.18) is quite complicated (for details see ^[19]).

²⁾When only direct transitions are taken into account, we obtain

$$\exp \left\{ \left[-\mu - \frac{m_h}{m+m_h} (E_g - \hbar\omega) \right] T^{-1} \right\}.$$

³⁾Similarly, at low temperatures the absorption mechanism representing transitions with simultaneous phonon absorption is quenched out.

⁴⁾The temperature of the diffusion quenching in n-GaAs is of the order of 900°K . Estimates show that in this energy region the correlation in the distribution of the impurities does not lead to a replacement of (3.18) by (3.72).

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