

## IMPURITY BAND AND CONDUCTIVITY OF COMPENSATED SEMICONDUCTORS

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A theory is developed for calculating the activation energies  $\epsilon_1$  and  $\epsilon_3$  for impurity conductivity in strongly compensated semiconductors. The case of weak doping is considered when the broadening of the impurity band is classical. In investigations of the structure of the impurity band and in the determination of the Fermi level, the screening of the random potential by the electrons on the impurities should be taken into account. At low temperatures, the screening differs significantly from the bias screening. This is the gist of the difficulty of the problem. It is demonstrated that for sufficiently large compensation the quantities  $\epsilon_1$  and  $\epsilon_3$  are related by the equation  $\epsilon_1 = E_B + \epsilon_3$ , where  $E_B$  is the ionization energy of the impurity. With increase of degree of compensation  $K$ , the quantity  $\epsilon_3$  grows like  $(1 - K)^{-1/3}$ ; with increasing concentration, it grows like  $N_D^{1/3}$ . The theory is compared with the experiment.

## 1. INTRODUCTION

AS is well known, there exist methods of preparing semiconductors with very close donor and acceptor concentrations ( $N_D \approx N_A$ ). For example, in [1] they used samples of germanium with a degree of compensation  $K = N_A/N_D = 0.995$ . The present paper is devoted to a study of the structure of the impurity band for large degrees of compensation ( $1 - K \ll 1$ ).

We assume for concreteness that the semiconductor is of the n-type, i.e.,  $N_D > N_A$ . Then each acceptor receiving an electron from the donor becomes negatively charged. The excess electrons with concentration  $n = N_D - N_A$  are located either on the donors or in the conduction band. They are acted upon by the field of a large number of negatively charged acceptors and by almost the same number of positively charged donors. This field determines the region of localization of the electrons, the depth of their Fermi level, and consequently the conductivity activation energy.

In this paper we consider only the case of weak doping, when  $N_D a^3 \ll 1$ , where  $a$  is the Bohr radius of the donor impurity. (As applied to Ge, for example, this means  $N_D \ll 5 \times 10^{18} \text{ cm}^{-3}$ .) In this case the impurity band is separated from the conduction band and at sufficiently low temperatures all the excess electrons are on the donors. As is well known, the dependence of the electric conductivity of such samples on the temperature contains two exponential sections. The high-temperature section, characterized by an activation energy  $\epsilon_1$ , is connected with the spilling of the electrons into the conduction band, and the low-temperature one, with activation energy  $\epsilon_3$ , is due to jumps over the impurity band.<sup>[2, 3]</sup> If we disregard the random field of the charged impurities, then at zero temperature the Fermi energy  $\mu$  (reckoned from the bottom of the conduction band) coincides with the binding energy  $E_B$  of the impurity center. It is obvious that in this approximation  $\epsilon_1 = E_B$ . In the field of the impurities, the electrons are distributed in such a way that their energy is minimal, i.e., in places with positive potential. As a result of this, the Fermi level turns out to be in the forbidden band at

a depth larger than  $E_B$ . The smaller the electron concentration, the weaker do they smooth out with their charge the potential relief, and the deeper the drop of the Fermi level.

In Sec. 2 we find the order of magnitude of this drop and its dependence on the degree of compensation. To find the numerical coefficient it is necessary to solve the parameterless equation obtained in Sec. 3. In Sec. 4 and Sec. 5 it is shown that the drop of the Fermi level leads to an increase of the activation energy with increasing degree of compensation. If  $(1 - K) \ll 1$ , the relation  $\epsilon_1 = E_B + \epsilon_3$  should be satisfied. In order of magnitude,  $\epsilon_3$  coincides with the drop of the Fermi level. A mathematical procedure is also proposed, which makes it possible to determine accurately  $\epsilon_1$  and  $\epsilon_3$ .

2. POSITION OF THE FERMI LEVEL  
(QUALITATIVE CONSIDERATIONS)

In the case of weak doping ( $N_D a^3 \ll 1$ ), the impurity states corresponding to neighboring atoms do not overlap. Therefore the wave function of the electron on the impurity practically does not differ from the wave function of the isolated impurity atom, and the potential of the remaining impurities can be regarded as slowly varying and as producing a classical level shift. At first glance it may appear that if the number of electrons is small, they do not distort greatly the impurity potential. Then it might be possible to determine the Fermi level of the electrons by assuming that they are in an external field of randomly disposed impurities, i.e., to use the single-electron approximation. The first complication that arises here consists in the fact that the mean-squared potential of randomly distributed Coulomb centers diverges at large distances. It is therefore necessary to recognize that even a few electrons screen the fluctuation potential. We are interested in the case when the temperature  $T$  (in energy units) is small compared with  $E_B$ , so that the number of electrons in the conduction band is very small. Then the screening is due to the redistribution of the electrons over the donors. If the average spread of the donor levels is small com-

pared with  $T$ , then the impurity band can be regarded in the first approximation as infinitesimally narrow and in the case of strong compensation we have

$$\mu = -E_B + T \ln(n/N_D). \quad (1)$$

From (1) we see that the Fermi level lies much lower than the impurity band and the probability of occupying a donor located at the point  $\mathbf{r}$  is  $\exp\{[\mu + e\varphi(\mathbf{r})]/T\}$ , where  $\varphi(\mathbf{r})$  is the potential produced at this point by the remaining impurities, and  $e$  is the absolute magnitude of the electron charge. If  $e\varphi/T \ll 1$ , then the Poisson-Boltzmann equation becomes linearized, and this leads to Debye screening of the potential of each impurity at a distance  $r_0^0 = (T\kappa/4\pi ne^2)^{1/2}$  ( $\kappa$  is the dielectric constant). Thus, in this case the electrons redistributed over the donors screen the impurity charge in the same manner as if they were free. The mean-square potential of the randomly disposed screened impurities, characterizing the width of the impurity band, is determined by the formula<sup>[4]</sup>

$$\gamma(r_0) = 2\sqrt{2\pi} \frac{e^2}{r_0\kappa} (N_D r_0^3)^{1/2}.$$

We see therefore that the condition for the applicability of (1) and of the Debye screening  $\gamma(r_0)/T \ll 1$  is satisfied when

$$T \gg \mu_0, \quad \mu_0 = \frac{e^2}{\kappa} \frac{N_D^{1/3}}{n^{1/3}}. \quad (2)$$

We now put  $T = 0$ . In this case the electrons occupy the deepest regions of the potential relief up to a level  $\mu$ . The electrons smooth out the relief somewhat, but since the electron concentration is small compared with the impurity concentration, their density remains essentially inhomogeneous. It is obvious that such a screening of the impurity potential differs strongly from the Debye screening. This constitutes the main difficulty of the problem in question. The problem of nonlinear screening of such a system was first formulated in<sup>[5]</sup>. However, the solution given in<sup>[5]</sup> contains an arbitrary assumption concerning the character of the correlation of the charged impurities. Therefore the result obtained in<sup>[5]</sup> differs significantly from ours.

We present qualitative considerations that make it possible to determine the Fermi energy in this case. The impurity potential contains fluctuations of all scales. Let us find the fluctuations producing potential wells in which one could place all the electrons in a way as to make their energy minimal. To this end we break up the crystal into regions with linear dimension  $R$ . The mean-square fluctuation of the number of impurities in each region is of the order of  $(N_D R^3)^{1/2}$ . In half of the regions the potential is raised, and in half of them it is lowered by an amount on the order of

$$\frac{\gamma(R)}{e} = \frac{e}{R\kappa} (N_D R^3)^{1/2}.$$

This means that the fluctuations of the impurities of scale  $R$  are capable of lowering the electron energy by an amount  $\gamma(R)$ . This amount increases without limit with increasing  $R$ . One must not forget, however, that in each of the considered potential wells there should be located  $nR^3$  excess electrons coming from regions with increased energy. Therefore the indicated lowering of

the potential  $\gamma(R)$  exists in reality only if  $(N_D R^3)^{1/2} > nR^3$ , i.e.,  $R < R_C$ , where

$$R_C = N_D^{1/3}/n^{2/3}. \quad (3)$$

The potential of large-scale fluctuations is smoothed by the electrons and such fluctuations are not effective. Thus, the main lowering of the electron energy is produced by fluctuations of scale  $R_C$ , and the size of this lowering is  $\gamma(R_C) = \mu_0$ , where  $\mu_0$  is defined in (2). For the Fermi level we obtain here

$$\mu = -E_B - \alpha_1 \mu_0, \quad (4)$$

where  $\alpha_1$  is a numerical factor ( $\alpha_1 > 0$ ).

In the derivation of (4) we have considered fluctuations close to the mean values. Of course, fluctuations with  $R < R_C$  can also produce a lowering of the potential by an amount on the order of  $\mu_0$ , but the probability of such deep fluctuations is exponentially small, and they can be disregarded.

The foregoing reasoning is applied to Gaussian fluctuations that include a large number of impurities. The probability of producing a potential well by non-Gaussian fluctuation of the concentration of the donors is proportional to  $\exp\{-Z \ln(Z/N_D V)\}$ , where  $Z$  is the number of donors participating in the fluctuations and  $V$  is the volume of the fluctuation. We see that this probability is the larger, the smaller  $Z$  (see also Fig. 1 of<sup>[4]</sup>). Thus, among the nonGaussian fluctuations, the most natural ones consist of the coming together of two donors to a distance  $R \ll N_D^{-1/3}$ . If in this case  $R \gg a$ , then the energy of the ground state of the electron in such a system is

$$\varepsilon(R) = -E_B - e^2/\kappa R. \quad (5)$$

We note, however, that when  $T = 0$  only one electron can sit on a pair of donors, since the binding energy of the second electron is  $E_B$ , which certainly is less than the depth by which the Fermi level drops. The density  $\rho(\varepsilon)$  of the electronic states is obtained by elementary calculation of the number of donor pairs with the aid of the function  $R(\varepsilon)$  defined in (5):

$$\rho(\varepsilon) = \frac{4\pi R^2}{2} \frac{dR}{d\varepsilon} N_D^2 = \frac{2\pi e^8 N_D^2}{(\varepsilon + E_B)^4 \kappa^2} \quad (6)$$

Of course, this formula is valid if an important role in (5) is played by  $R$  satisfying the inequality  $a \ll R \ll N_D^{-1/3}$ , i.e., when

$$e^2 N_D^{1/3}/\kappa \ll -\varepsilon - E_B \ll E_B.$$

Calculating the Fermi energy at  $T = 0$  with the aid of (6), we obtain (4) with  $\alpha_1 = (2\pi/3)^{1/3}$ . Thus, the donor pairs and the Gaussian fluctuations make a comparable contribution to the lowering of the Fermi energy, and the exact theory should take into account both mechanisms. However, if the degree of compensation is such that  $\mu_0 = E_B$ , only Gaussian fluctuations are important, since the donor pair cannot produce such a lowering, and the probability of coming together of a large number of donors to small distances is exponentially small.<sup>[4]</sup> The final results of the foregoing reasoning is that when  $T = 0$  the Fermi energy is given by formula (4).

Let us investigate now the manner of the transition from (4) to (1) with increasing temperature. When  $T = 0$

there are in a unit volume  $n$  states with energy below the Fermi energy and  $N_D$  states lying at a height on the order of  $\mu_0$  above the Fermi energy. We can therefore assume that the electrons are mainly below the Fermi energy if  $T \ll T_D \equiv \mu_0 / \ln(N_D/n)$ . In other words,  $T_D$  is the temperature of the degeneracy of the electrons in the impurity band. The result (4) is valid only when  $T \ll T_D$ . In the region  $T_D \ll T \ll \mu_0$ , the Fermi level is determined mainly by formula (1). However, since the impurity band is smeared out by an amount on the order of  $\mu_0$ , we have

$$\mu = -E_B + T \ln(n/N_D) - \alpha_2 \mu_0, \quad (7)$$

where  $\alpha_2$  is a numerical factor ( $\alpha_2 > 0$ ).

### 3. FUNDAMENTAL EQUATIONS

We now proceed to construct a quantitative theory for  $T \ll T_D$  and  $\mu_0 \ll E_B$ . We write down the Poisson equation for the potential  $\varphi$  averaged over fluctuations having a scale smaller than  $L$ , with  $n^{-1/3} \ll L \ll R_C$ , where  $R_C$  is defined by (3):

$$\Delta\varphi = -4\pi e(N_D(\mathbf{r}) - N_A(\mathbf{r}) - n(\mathbf{r})). \quad (8)$$

Here  $N_D(\mathbf{r})$ ,  $N_A(\mathbf{r})$ , and  $n(\mathbf{r})$  are the mean values, in the sense indicated above, of the concentrations of the donors, acceptors, and electrons. To calculate  $n(\mathbf{r})$  it is necessary to know the density of states  $\varphi(\epsilon, \mathbf{r})$  produced by fluctuations with a scale smaller than  $L$  in the vicinity of the point  $\mathbf{r}$ . Since the scale of variation of  $\varphi(\mathbf{r})$  is large compared with  $L$ , the density of states  $\varphi(\epsilon, \mathbf{r})$  should be connected with  $\varphi(\mathbf{r})$  locally. As already mentioned, we are interested in the lowering of the potential by an amount on the order of  $\mu_0$ . The probability of producing such a drop as the result of a Gaussian fluctuation with dimension  $L$  is proportional to  $\exp(-\mu_0^2/\gamma^2(L))$ , where  $\gamma(L) = e^2(NL^3)^{1/2}/\kappa L$ . Since by definition  $L \ll R_C$ , such a probability is exponentially small and can be disregarded. The density of the states produced by non-Gaussian fluctuations is given by formula (6), in which the energy  $\epsilon$  should be reckoned from the bottom of the conduction band, shifted by the large-scale fluctuations by an amount  $-e\varphi(\mathbf{r})$ . Thus,  $\rho(\epsilon, \mathbf{r})$  is obtained from (6) by replacing  $\epsilon$  with  $\epsilon + e\varphi(\mathbf{r})$ . We then have

$$\begin{aligned} n(\mathbf{r}) &= \int_{-\infty}^{\mu} \rho(\epsilon, \mathbf{r}) d\epsilon = 2\pi e^{\mu_0} \kappa^{-3} N_D^2 \int_{-\infty}^{\mu} \frac{d\epsilon}{(\epsilon + e\varphi + E_B)^4} \\ &= -\frac{2\pi}{3} N_D^2 e^{\mu_0} \kappa^{-3} (\mu + E_B + e\varphi)^{-3}. \end{aligned} \quad (9)$$

We introduce the dimensionless variables

$$\chi = -\left(\frac{3}{2\pi}\right)^{1/2} \frac{e\varphi}{\mu_0}, \quad \delta = -\frac{\mu + E_B}{\mu_0} \left(\frac{3}{2\pi}\right)^{1/2}, \quad (10)$$

$$\mathbf{x} = 2^{1/2} 3^{1/2} \pi^{1/2} \mathbf{r} / R_C, \quad (11)$$

$$f = [(N_D(\mathbf{r}) - N_D) - (N_A(\mathbf{r}) - N_A)] / (N_D - N_A). \quad (12)$$

Substituting (9)–(12) in (8), we obtain an equation

$$\Delta_{\mathbf{x}} \chi = f + 1 - \frac{1}{(\chi + \delta)^3}, \quad (13)$$

which is valid when  $\chi > -\delta$ . Since we assume the impurity distribution to be uncorrelated, it follows from

the definition (12) that  $f(\mathbf{x})$  is a Gaussian random function with a correlator

$$\langle f(\mathbf{x}), f(\mathbf{x}') \rangle = 2^{1/2} 3^{1/2} \pi \delta(\mathbf{x} - \mathbf{x}'). \quad (14)$$

(Strictly speaking, the  $\delta$  function in (14) is spread out over a distance  $\Delta \mathbf{x} \approx L/R_C \ll 1$ .) To determine  $\delta$  it is necessary to specify the function  $f$  in a region with linear dimension  $X \gg 1$  and to stipulate that Eq. (13) have a solution with a zero total charge of the region (integral of the right-hand side of (13)) and with a potential that tends to zero at infinity. It is clear that when  $X \gg 1$  the chemical potential  $\delta$  does not depend on the form of  $f$ . The corresponding numerical calculations can be performed with a computer. However, from the fact that Eqs. (13) and (14) do not contain parameters, it follows that  $\delta \approx 1$ . We have thus obtained the result (4) with  $\alpha_1 = \delta(2/3\pi)^{1/2}$ .

We investigate now the distribution of the potential  $\chi$ . We introduce the function  $F(\chi)$ , which represents the probability density of the potential  $\chi$ . This function should satisfy the normalization and neutrality conditions

$$\int_{-\infty}^{\infty} F(\chi) d\chi = 1, \quad \int_{-\infty}^{\infty} \frac{F(\chi) d\chi}{(\chi + \delta)^3} = 1. \quad (15)$$

Averaging (13) over all the possible  $f$  and recognizing that  $\chi = 0$  at infinity, we easily obtain one more condition:

$$\langle \chi \rangle = \int_{-\infty}^{\infty} \chi F(\chi) d\chi = 0. \quad (16)$$

It follows from (16) that  $\delta > 0$ , i.e.,  $\alpha_1 > 0$ , and the Fermi level lies below the unperturbed Bohr level.

Of course,  $F(\chi)$  cannot be calculated without an exact solution of (13), but we can investigate the asymptotic properties of this function. It is shown in the Appendix that as  $\chi \rightarrow -\delta$  the function  $F(\chi) \rightarrow 0$  no slower than  $(\chi + \delta)^5$ , and when  $\chi \gg 1$  we have  $F(\chi) \sim \exp(-2/3 \chi^{3/2}/\sqrt{3})$ . Therefore the integrals (15) and (16) converge. The convergence of the second integral in (15) at the lower limit denotes that an important role is played in the calculation of the Fermi level by regions in which  $\chi + \delta$  is of the order of unity. It follows therefore that the electrons are localized on the donor pairs with a classical level shift on the order of  $\mu_0$ . This justifies the use of formula (9). The rapid decrease of  $F(\chi)$  as  $\chi \rightarrow -\delta$  denotes that the large-scale fluctuations cannot drop the Bohr level below the Fermi level, since the local concentration of the electrons (9) increases strongly in this case and smoothes out the potential well.<sup>1)</sup>

### 4. ACTIVATION ENERGY $\epsilon_1$

As already mentioned, at not too low temperatures, the electric conductivity is due to the electrons thrown from the impurities into the conduction band. The corresponding activation energy is customarily denoted by  $\epsilon_1$  (see Fig. 1). To calculate  $\epsilon_1$  it is very important to

<sup>1)</sup>This circumstance was not taken into account in [6], and led to the incorrect conclusion that the concentration of the electrons in the conduction band remains finite at  $T = 0$  as a result of the large-scale fluctuations.

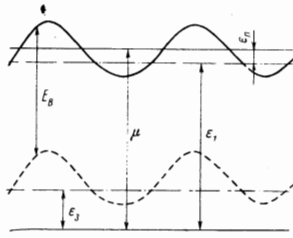


FIG. 1. Energy scheme of a compensated semiconductor. The wave lines (solid and dashed) represent the bottom of the conduction band and the energy of the ground state of the impurity, which duplicate the course of the large-scale potential  $\varphi(\mathbf{r})$ . The upper solid line represents the mean value of the energy of the bottom of the conduction band, which coincides with the energy of the bottom of the unperturbed band. The lower solid line represents the Fermi level. The dash-dot lines show the flow-through levels in the conduction and in the impurity bands.

bear in mind that the bottom of the conduction band duplicates the course of the large-scale fluctuations of the potential  $\varphi(\mathbf{r})$ . Indeed, the amplitude of the fluctuations is of the order of  $\mu_0$ , and the characteristic dimension is  $R_C$ . The tunnel transparency of such a relief contains

$$\exp(-R_C \sqrt{m\mu_0}/\hbar) = \exp\{-(N/n)^{1/3}(Na^3)^{-1/3}\}, \quad (17)$$

i.e., it is negligibly small. Therefore the electron can be regarded classically in this potential.

In order for an electron with energy  $\epsilon$  to make a contribution to the static conductivity it is necessary that there exist paths passing through the entire crystal, and at each point of such a path the potential energy of the electron  $-e\varphi(\mathbf{r})$  must be smaller than  $\epsilon$ . Obviously at small  $\epsilon$  there exist no such paths, i.e., the regions with potential energy smaller than  $\epsilon$  are not interconnected. To contrary, at large  $\epsilon$  there are many such paths. We introduce the energy  $\epsilon_p$  such that when  $\epsilon > \epsilon_p$  there exist single-connected regions with potential energy smaller than  $\epsilon$ , piercing the entire crystal, and at  $\epsilon < \epsilon_p$  there are no such regions. The probability-theory problem of determining  $\epsilon_p$  should be solved with the aid of Eqs. (13) and (14). Since these equations do not contain parameters, it is obvious that  $\epsilon_p = \beta\mu_0$ , where  $\mu_0$  is defined in (2), and  $\beta$  is a universal numerical constant that does not depend on any crystal parameters. This problem can be formulated in analogy with the well known problem of flow of a liquid through a random labyrinth.<sup>[7]</sup> Let us imagine in the crystal a three-dimensional periodic lattice with period  $l$ . We call the nodes at which the potential energy is smaller than  $\epsilon$  nodes of type A, and the remainder nodes of type B. It is obvious that the fraction of nodes of type A is

$$p_A(\epsilon) = \int_{-\infty}^{(\epsilon/\mu_0)(3/2\pi)^{1/3}} F(\chi) d\chi. \quad (18)$$

We shall say that two nodes of type A are connected if there exists between them a path over the lattice such that each node on the path is a node of type A. It is required to find such an energy  $\epsilon_p(l)$  that when  $\epsilon > \epsilon_p(l)$  the probability of an arbitrary node of type A to be connected with an infinite number of nodes of type A is different from zero, and at  $\epsilon < \epsilon_p(l)$  this probability is equal to zero. The flow-through energy of interest to us is defined as  $\lim_{l \rightarrow 0} \epsilon_p(l)$ . At a fixed  $l$ , our problem dif-

fers from the classical flow-through problem only in that the distribution of the nodes of type A and B in the lattice is not random. Indeed, as follows from (13), in the case of a random distribution of the impurities the distribution of the potential is correlated over a distance  $R_C$ , i.e., when  $l < R_C$  the nodes of one type are arranged as a rule in clusters with dimension  $R_C$ . It is obvious that when  $l \ll R_C$  the energy  $\epsilon_p(l)$  does not depend on  $l$  and the limit of interest to us exists. We can estimate once more  $\beta$  by using the solution of the flow-through problem.<sup>[7]</sup> It is clear from the foregoing that  $\epsilon_p$  is of the same order as  $\epsilon_p(l)|_{l=R_C}$ . On the other hand, we

can assume approximately that at  $l = R_C$  there is no correlation in the arrangement of the nodes, i.e., the nodes of type A are distributed randomly in the lattice with a probability (18). Then it follows from<sup>[7]</sup> that  $\epsilon_p$  is determined by the equation  $p_A(\epsilon_p) = p_C$ , where  $p_C$  is a number somewhat smaller than 0.3. From this we again obtain  $\epsilon_p = \beta\mu_0$ , and since  $p_C < 1/2$ , it is quite probable that  $\beta < 0$ . The probability that an arbitrary node of type A is connected with an infinite number of nodes of type A, as seen from<sup>[7]</sup>, increases to a value on the order of unity when  $p_A$  exceeds  $p_C$  very slightly. As applied to our problem, this means that the number of paths piercing the crystal becomes large when  $(\epsilon - \epsilon_p)\epsilon_p^{-1} \ll 1$ . Therefore at low temperatures the main contribution to the conductivity is made by electrons with energy barely exceeding  $\epsilon_p$ . Consequently, the activation energy is  $\epsilon_1 = \epsilon_p - \mu$ , or, substituting (4), we have

$$\epsilon_1 = E_B + (\beta + \alpha_1)\mu_0. \quad (19)$$

According to the proof in Sec. 3, the potential energy of the electron cannot be smaller than  $-\alpha_1\mu_0$ . It is therefore certainly clear that the flowthrough level  $\epsilon_p$  lies above the energy  $-\alpha_1\mu_0$  by an amount on the order of  $\mu_0$ . It follows therefore that  $\beta + \alpha_1 > 0$ , i.e.,  $\epsilon_1 > E_B$ . We have proved that the activation energy  $\epsilon_1$  exceeds  $E_B$  by an amount on the order of  $\mu_0$ , which increases with increasing degree of compensation like  $(1-K)^{-1/3}$ , and increase like  $N_D^{1/3}$  with increasing concentration of the main impurities at fixed  $K$ .

The coefficients  $\alpha_1$  and  $\beta$  must be calculated with a computer in accordance with the recipe indicated above. If the electrons in the impurity band are not degenerate ( $T > T_D$ ) then, as seen from (7), it is necessary to replace the constant  $\alpha_1$  in (19) by  $\alpha_2$ . The recipe for calculating  $\alpha_2$  will be given in a succeeding paper.

The experimental data given in the review<sup>[3]</sup> and also in<sup>[8,9]</sup> show that in strongly compensated Ge the activation energy  $\epsilon_1$  exceeds  $E_B$  and increases with increasing degree of compensation. For example, from the data of<sup>[3]</sup>, in a p-type sample with  $K = 0.91$  and an acceptor (gallium) concentration  $N_A = 2.7 \times 10^{15} \text{ cm}^{-3}$  the activation energy is  $\epsilon_1 \approx 13 \text{ meV}$ , and  $E_B = 10.8 \text{ meV}$ . From the data of<sup>[8]</sup>, in an n-type sample with  $K = 0.92$  and a donor (antimony) concentration  $N_D = 5.4 \times 10^{16} \text{ cm}^{-3}$ , the activation energy is  $\epsilon_1 = 13 \text{ meV}$ , whereas  $E_B = 9.6 \text{ meV}$ . However, the aforementioned data do not make it possible to determine the law of variation of  $\epsilon_1$  with  $(1-K)$ . To this end it is necessary to perform experiments with samples having a larger degree of compensation. Very high activation energies

( $\epsilon_1 \approx 100$  meV) were observed in compensated n-Ge in [10]. The dependence of  $\epsilon_1$  on  $(1 - K)$  turns out to be stronger than the one resulting from our theory. This possibly is due to the correlation in the arrangement of the impurities, which arises upon annealing and which changes in these experiments together with  $(1 - K)$ .

### 5. THE ACTIVATION ENERGY $\epsilon_3$

Competing with the above-discussed mechanism of electric conductivity through the conduction band is the conductivity through the impurity band. The probability of jumping from one impurity atom to another contains a very small factor  $\exp -2R/a$ , where  $R$  is the distance between impurities. Therefore the jump mechanism wins only at sufficiently low temperatures.

The problem of calculating the jump resistance of the crystal reduces to the problem of the resistance of a three-dimensional random grid, the nodes of which are connected with one another by elements with their resistance proportional to  $\exp 2R/a$ , where  $R$  is the distance between these nodes. This resistance was investigated in greatest detail by Miller and Abrahams. [12] Their calculations can be interpreted in the following manner. We fix a certain chain of donors passing through the entire crystal, and we calculate its resistance. Since the elements of the chain are connected in series, the main contribution to the resistance is made by sections with large distances between the neighboring donors ( $R \gg N_D^{-1/3}$ ). The probability density of the fact that the nearest neighbor of the fixed donor is located at a distance  $R$  from it is proportional to  $\exp(-\frac{4}{3}\pi NR^3)$  ( $R \gg N_D^{-1/3}$ ). Therefore the contribution to the resistance of the chain from the elements of length  $R$  is proportional to

$$\exp(-\frac{4}{3}\pi N_D R^3) \exp(2R/a). \quad (20)$$

This quantity has a sharp maximum at  $R_m = (2\pi a N)^{1/2}$ . Thus, the main contribution to the resistance of the chain is made by elements with length close to  $R_m$ . Substituting the expression for  $R_m$  in (20) and assuming that all the chains have the same resistance, we obtain for the resistivity  $\rho$  of the crystal

$$\rho \sim \exp\{1.09(R_d/a)^{3/2}\}, \quad R_d = (\frac{2}{3}\pi N_D)^{1/2}. \quad (21)$$

This is the main result of Miller and Abrahams.

It is possible to show, however, that there always exists a considerable number of chains that go around the rarefied places and have for this reason a much smaller resistance. To this end we ascertain the probability  $P$  of the fact that an arbitrary donor is connected with an infinite number of other donors by chains consisting of only elements with length smaller than  $R$ . This problem is among the aforementioned probability-theory flow problems. It was solved in [11] by the Monte Carlo method with a computer. The result is that  $P = 0$  so long as  $p \equiv \frac{4}{3}\pi N_D R^3 < 2.32$ . When  $p > 2.32$  the probability differs from zero and increases very rapidly, reaching a value on the order of unity at  $p = 2.32 \approx 0.05$ . Thus, at a fixed concentration  $N_D$  almost each donor belongs to a chain passing through the entire crystal and consisting of elements with length shorter than  $tR_d$ , where  $t$  slightly exceeds  $(2.32)^{1/3} = 1.32$ . Taking these chains into account, we obtain for the resistivity of the crystal

$$\rho \sim \exp\{2tR_d/a\}. \quad (22)$$

Since  $R_d \gg a$ , the resistivity of the crystal is determined not by formula (21) but by formula (22). Our result (22) differs noticeably from the formula  $\rho \sim \exp(1.46R_d/a)$  obtained by Twose [12] using the approximate method proposed by Pippard for averaging the resistances of the chains.

In our preceding reasoning we calculated the resistance of the chain under the assumption that the probability of filling the donors comprising the chain with electrons does not contain an exponentially small factor. As already mentioned, the levels of most donors are raised above the Fermi level by an amount on the order of  $\mu_0$  and have a scatter of the same order. Therefore formula (22) is valid only at high temperatures  $T \gtrsim \mu_0$ . At low temperatures ( $T \ll \mu_0$ ) the optimal chains should pass through regions with the lowest possible donor-level energy in a field of the large-scale potential  $\varphi(\mathbf{r})$ . We shall characterize each chain by the quantity  $\epsilon_{\max}$ , which represents the energy of the highest donor level encountered in this chain. Then it follows from the results of Sec. 1 that in a potential  $\varphi(\mathbf{r})$  there exist no chains with  $\epsilon_{\max} + E_B < \epsilon_p$  and there exist a large number of chains in which  $\epsilon_{\max} + E_B$  slightly exceeds  $\epsilon_p$ . (Here  $\epsilon_p$  is the flow-through energy defined in Sec. 4.) Therefore at sufficiently low temperatures the resistance will be determined by chains having  $\epsilon_{\max}$  close to  $\epsilon_p - E_B$ . The principal term of the argument of the exponential in the expression for the resistance of such a chain is determined by the resistance of the sections with  $\epsilon \approx \epsilon_{\max} = \epsilon_p - E_B$ . As a result we have

$$\rho \sim \exp(\epsilon_3/T) \exp(2tR_d/a), \quad (23)$$

$$\epsilon_3 = \epsilon_n - E_p - \mu = (\beta + \alpha)\mu_0. \quad (24)$$

The first factor in (23) is the probability of filling with electrons the region with energy  $\epsilon_{\max} = \epsilon_p - E_B$ . The second factor is the probability of the jump between the donors in the region where the energy is  $\epsilon \approx \epsilon_{\max}$ . The coefficient  $t_1$ , generally speaking, can be different from  $t$ , but it is nonetheless of the order of unity.

Comparing (19) and (24), we obtain a relation between  $\epsilon_1$  and  $\epsilon_3$ :

$$\epsilon_3 = \epsilon_1 - E_B. \quad (25)$$

As is clear from the derivation of (25), this relation should be satisfied only in the case of sufficiently strong compensation ( $(1 - K)^{1/3} \ll 1$ ).

With decreasing temperature, the conductivity through the flow level, described by formula (23), should be lower than the conductivity through the Fermi level. This conductivity is due to jumps between donor pairs with energy close to the Fermi energy. The average distance between such pairs is of the order of  $n^{-1/3}$ . Therefore the conductivity over the Fermi level becomes comparable with the conductivity over the flow level at  $T \approx T_c \equiv \mu_0(na^3)^{1/3}$ . When  $T \ll T_c$ , the conductivity over the Fermi level predominates. The activation energy in this region decreases with temperature. [13] In the experiments analyzed below, no temperatures lower than  $T_c$  were reached.

It follows from (24) that  $\epsilon_3 \sim (1 - K)^{-1/3} N_D^{1/3}$ . In Fig. 2 we compare the dependence of  $\epsilon_3$  on  $K$ , which is predicted by us, with the experimental data given in

Fig. 8 of the review [3]. The agreement should be regarded as satisfactory, although there is no complete assurance that the degree of compensation of the investigated samples satisfies sufficiently well the conditions for applicability of our theory. As seen from Fig. 2 and as noted in [3], the theory of Miller and Abrahams describes poorly the experimental data at  $(1 - K) \ll 1$ . The point is that no account is taken in this theory of the dropping of the Fermi level as a result of the formation of donor pairs and large-scale fluctuations.

Let us discuss now the experimental data pertaining to the second factor in (23). This factor determines the pre-exponential factor  $\rho_3$  in the dependence of  $\rho$  on  $T^{-1}$ . It follows from (23) that  $\ln \rho_3 \sim R_d$ . We know of no experiments which make it possible to verify this circumstance at large degrees of compensation. It is clear from the foregoing, however, that this conclusion is not sensitive to the degree of compensation.

Fritzsche [14] found that in p-Ge with  $K = 0.4$  the dependence of  $\ln \rho_3$  on  $R_d$  is linear. A linear dependence was obtained also by Mott, [3] who analyzed the data of [15] for n-Ge. These results agree with (22) and (23).

Another experimentally established fact is the weak increase of  $t_1$  with increasing degree of compensation. [3] We present a possible qualitative explanation of this phenomenon. As already mentioned, it is most probable that  $\epsilon_p < 0$ . If this is not so, then regions with energy  $\epsilon = \epsilon_{\max}$  are in potential wells of depth on the order of  $\mu_0$ . As mentioned in Sec. 2, in such regions the concentration of the donors exceeds the average value by an amount on the order of  $n$ . Since  $t_1 R_d$  in (23) is determined by the average distance between the donors precisely in the region with  $\epsilon = \epsilon_{\max}$ , it is necessary to replace  $t_1$  in (23) by  $t_1 [1 - \nu(1 - K)]$ , where  $\nu$  is a coefficient on the order of unity. Under the conditions of applicability of this expression  $(1 - K) \ll 1$  the correction term in the argument of the exponential is small, but it is sufficient to explain the effect. For final conclusions, however, it is necessary to determine the sign of  $\beta$ .

## APPENDIX

We write  $F(\chi)$  in the form of a functional integral over all  $f$ :

$$F(\chi) = \frac{\int \delta(\chi - \chi\{f\}) e^{-\alpha(f)} Df}{\int e^{-\alpha(f)} Df}, \quad (\text{A.1})$$

where

$$\Omega\{f\} = \frac{1}{2^{3/2} 3^{1/2} \pi} \int f^2 dx, \quad (\text{A.2})$$

$\chi\{f\}$  is a functional representing the solution of (13) at a fixed point. As we shall show below,  $F(\chi)$  is exponentially small when  $\chi \gg 1$ . Therefore the principal term in  $\ln F(\chi)$  can be found from the formula [16]

$$\ln F(\chi) = -\Omega\{f\}, \quad (\text{A.3})$$

where  $\tilde{f}$  is a function realizing the extremum of the functional  $\Omega\{f\}$  under the additional condition that the potential  $\chi\{f\}$  at a certain point is equal to  $\chi$ . We place the origin at this point and recognize that in view of the

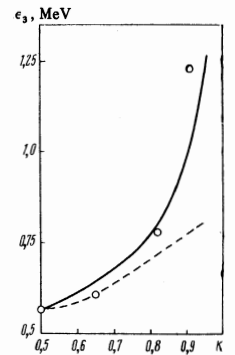


FIG. 2. Dependence of  $\epsilon_3$  on  $K$ .  $\circ$ —experimental points, taken from [3]. Solid line—plot of the function  $A(1-K)^{-1/3}$ , with  $A$  chosen such as to make the plot pass through the experimental point at  $K = 0.5$ . Dashed line—result of theory [2].

spherical symmetry of the problem the extremal function does not depend on the angles. [16] In the region where  $\chi \gg 1$ , there are no electrons, i.e., the last term in (13) can be neglected. The electrons appear only at a distance  $x_0 \gg 1$  from the center of the fluctuation, at which the potential decreases almost to zero. They neutralize the fluctuation rapidly, so that the region where there are electrons gives a small contribution to the potential of the center of the fluctuation  $\chi\{f\}$ . Thus, in spherical coordinates we have

$$\chi\{f\} = - \int_0^{\infty} (1+f) x dx, \quad (\text{A.4})$$

with  $x_0$  determined by the condition

$$\int_0^{\infty} (1+f) x^2 dx = 0. \quad (\text{A.5})$$

The extremal function  $\tilde{f}$  is determined from the equation  $\delta(\Omega\{f\} + \beta\chi\{f\}) = 0$ , where  $\beta$  is a Lagrange multiplier which must be determined from the condition  $\chi\{\tilde{f}\} = \chi$ . In the variation of (A.4) it is necessary to take into account the variation of  $x_0$ , which is determined from (A.5). We ultimately obtain

$$\tilde{f} = - \frac{2\sqrt{2}\chi^{1/2}}{x} \left(1 - \frac{x}{x_0}\right), \quad x_0 = \sqrt{2}\chi^{1/2} \quad (\text{A.6})$$

Substituting (A.6) in (A.2) and (A.3) we obtain

$$F(\chi) \sim \exp(-2\chi^{1/2}/3\sqrt{3}). \quad (\text{A.7})$$

We now investigate the function  $F(\chi)$  near the termination point  $\chi = -\delta$ . We assume that the function  $f$  differs from zero in the region with linear dimension  $x_1$ . As seen from (A.1) and (A.2), in order for the probability of such a fluctuation not to have an exponential smallness, it is necessary that the function  $f(x)$  increase as  $x \rightarrow 0$  not faster than  $x^{-3/2}$ , in order to satisfy the condition  $f^2(x_1)x_1^3 \leq 1$ . On the other hand, when the potential is dropped by an amount  $\delta \approx 1$  it is necessary to have  $f(x_1)x_1^2 \leq 1$  (see (A.4)). These conditions yield  $x_1 \gtrsim 1$ . However, as seen from (13), fluctuations with a unit potential are screened by electrons at a unit distance. Therefore the only possibility of producing a unit drop in the potential with a non-exponentially small probability is a fluctuation with  $f(x_1) \approx 1$ ,  $x_1 \approx 1$ . The foregoing reasoning does not take into account the potential of the electrons. However, as seen from (13), as  $\chi \rightarrow -\delta$ , i.e., at the center of the fluctuation, the concentration of the electrons becomes very large. Therefore in order for the potential to have a minimum at the center, the function  $f$  at the center should be large. Let us investigate

the behavior of  $f$  and  $\chi$  near the center. When  $x \ll 1$  the function  $\chi$  can be represented in the form  $\chi = -\delta + \Delta\chi + Ax^n$ ,  $n > 0$ , where  $\Delta\chi$  and  $A$  are constants, and  $\Delta\chi \ll 1$ . Since  $\chi$  and  $f$  are of the order of unity when  $x \approx 1$ , we have  $A \approx 1$ . We substitute the expression for  $\chi$  in (13) and investigate it in the region  $x^n \gg \Delta\chi$ . It can be verified that a solution with  $A > 0$  exists only if  $f$  at the center increases no slower than  $x^{-3/2}$  so long as  $x > (\Delta\chi)^{1/n}$ . If  $f$  increases more rapidly than  $x^{-3/2}$ , then, as already mentioned, the lower limit of the integral in (A.2) is important, and the probability of such a fluctuation is small like  $\exp\{-(\Delta\chi)^p\}$ , where  $p < 0$ . Thus, the optimal function  $f$  increases at the center like  $x^{-3/2}$ . It is seen from (13) that in this case  $n = 1/2$  and consequently the volume of the region where  $(\chi + \delta) \approx \Delta\chi$  is of the order of  $(\Delta\chi)^6$ . An upper estimate for  $F(\chi)$  can be obtained by assuming that the obtained optimal fluctuations of unity dimension fill densely all of space. In this case the fraction of the volume in which  $(\chi + \delta) \approx \Delta\chi$  is of the order of  $(\Delta\chi)^6$ . Consequently as  $\chi \rightarrow -\delta$  the function  $F(\chi)$  decreases more rapidly than  $(\chi + \delta)^5$ .

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92