

HOPPING CONDUCTION IN LIGHTLY DOPED SEMICONDUCTORS (REVIEW)

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Translated from *Fizika i Tekhnika Poluprovodnikov*, Vol. 6, No. 7,

pp. 1197-1226, July, 1972

Original article submitted March 10, 1972

This review deals with hopping conduction under dc conditions. A new theory of hopping conduction, based on the percolation method, is put forward. This theory makes it possible to find the dependence of the resistance on the concentration and chemical nature of impurities. It also predicts the giant hopping piezoresistance of germanium and the giant positive magnetoresistance of Al₁₁Bi₁ crystals in the hopping conduction region. A theoretical analysis is made of the activation energy of hopping conduction in weakly and strongly compensated semiconductors. All the theoretical conclusions are compared in detail with the experimental results.

1. INTRODUCTION

A semiconductor is regarded as lightly doped if the impurity concentration N is such that the average distance between impurities $N^{-1/3}$ is greater than the Bohr radius a of the impurity ($Na^3 \ll 1$). Two charge-transport mechanisms operate in such a semiconductor. At relatively high temperatures the conduction is due to electrons which are ejected from impurity levels to the conduction band (to be specific, we shall assume that the impurities are donors). When the temperature is lowered, the number of electrons in the conduction band decreases rapidly and jumps of electrons from donor to donor increase in importance. These jumps occur because of the exponentially small overlap of the wave functions of two neighboring impurity states (free donors are usually present because of compensation). This type of conduction is known as the hopping process.

Experimental and theoretical investigations of hopping conduction carried out up to 1961 are discussed in detail in the well-known review of Mott and Twose [1]. During the last decade much new work has been published. In particular, many investigations deal with hopping conduction in lightly doped semiconductors under ac conditions (see, for example, [2, 3]). The hopping conduction ideas are frequently used in the interpretation of the ex-

perimental data obtained for crystalline, as well as amorphous semiconductors [4, 5]. In recent years it has become accepted that in strongly compensated semiconductors the hopping mechanism may be observed not only in the case of light doping but also under heavy doping conditions when $Na^3 \gg 1$ [6]. In the absence of compensation the electrons in a heavily doped semiconductor form an almost perfect Fermi gas and the conduction is of a metallic nature, i.e., the conductivity is high and does not vary strongly with temperature. When a heavily doped semiconductor is compensated by the introduction of impurities in amounts similar to those present initially, the metallic conduction is destroyed [7]. This happens because the electrons remaining in the conduction band collect into metallic droplets separated from one another by high and difficult to penetrate potential barriers. In other words, the electron sea dries out and leaves behind a few isolated lakes. If the temperature is sufficiently high, the electrons in such a system acquire thermal energy sufficient to overcome the potential barriers. However, at very low temperatures the electrons are highly unlikely to overcome the barriers and the conduction is due to the tunneling across the barriers, i.e., due to jumps from one potential well to another. This mechanism can be justifiably called the hopping

conduction. The difference between this mechanism and the hopping conduction in a lightly doped semiconductor is that the electron states before and after a jump do not belong to the same impurity but are due to fluctuations in the concentration of impurities which involve many impurities simultaneously.

We shall not discuss these new aspects of hopping conduction. We shall restrict our review to the investigations which deal with the dc hopping conduction in lightly doped semiconductors and with the dependence of this type of conduction on the concentration and chemical nature of the impurities and its dependence on the temperature, magnetic field, and pressure. The review will be based on a new theory of hopping conduction, which has been developed in a series of papers [8-12]. It follows from this theory that, in particular, the principal results of the well-known work of Miller and Abrahams [13] — which are frequently used in the analysis of experimental data — are in error. The new theory will be used to review the old data and to analyze the large amount of new experimental information on hopping conduction.

Let us start by recalling the principal experimental observations [1]. At sufficiently low temperatures the conductivity of a lightly doped semiconductor σ is of the form

$$\sigma = \rho_1^{-1} e^{-\frac{\varepsilon_1}{kT}} + \rho_3^{-1} e^{-\frac{\varepsilon_3}{kT}}, \quad (1)$$

where the first term represents the contribution of the "band" conduction and the second term the contribution of hopping conduction. At "intermediate" doping levels (in the case of germanium, these levels correspond to donor concentrations in the range $10^{16} < N_D < 10^{17} \text{ cm}^{-3}$) in a weakly compensated semiconductor, the conductivity has an additional term $\rho_2^{-1} e^{-\varepsilon_2/kT}$ ($\varepsilon_1 > \varepsilon_2 > \varepsilon_3$), whose origin is not yet fully understood. Traditionally, this term is called the third term. Most of our review will be restricted to impurity concentrations in which this third term $\rho_2^{-1} e^{-\varepsilon_2/kT}$ is negligible.

The necessary condition for the hopping conduction is the compensation. Let us assume that there are N_D donors and N_A acceptors ($N_A < N_D$) in a unit volume of a semiconductor. Then, at low temperatures the N_A acceptors will capture electrons and become negatively charged and the N_A donors will remain unoccupied, i.e., positively charged. The random potential of charged impurities leads to slight differences between the energies of the levels of the various donors, and the ab-

sorption of phonons is necessary in jumps from one donor to another. This is the reason for the activation-type temperature dependence of the hopping conductivity. The quantity ε_3 depends on the concentrations of the principal and compensating impurities, i.e., it depends on N_D and on N_A . However, the main dependence of the hopping conductivity on N_D is included in the factor ρ_3 . This factor increases exponentially with decreasing N_D and, therefore, it is convenient to write it in the form $\rho_3 = \rho_0 e^{f(N_D)}$. When N_D is altered by a factor of 30, the value of ρ_3 increases by a factor of 10^7 [1]. The exponential variation of ρ_3 is due to the fact that the probability of a jump W_{ij} of an electron from a donor i , located at the point \mathbf{r}_i , to a donor j , located at \mathbf{r}_j , is proportional to the square of the modulus of the overlap integral of the wave functions of the ground state of an electron at each of the donors [13]:

$$W_{ij} \propto \left| \int \psi_i(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} \right|^2. \quad (2)$$

We shall assume that the electron spectrum is isotropic, i.e., that the wave function of each donor is hydrogen-like and that it decreases at large distances in accordance with the law $\psi_i \propto \exp(-|\mathbf{r} - \mathbf{r}_i|/a)$, where $a = \hbar/(2m^*E)^{1/2}$ is the Bohr radius of the ground state; E is the experimentally determined ionization energy of the donor; m^* is the effective mass. Then, we find that

$$W_{ij} \propto e^{-\frac{2r_{ij}}{a}}, \quad (3)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the donors i and j . At low donor concentrations the average distance between donors is $N_D^{-1/3} \gg a$ and, therefore, the probability of a jump between neighboring donors is exponentially small and the resistivity ρ_3 is exponentially large.

We shall begin our review by presenting the theory of the quantity ρ_3 in the simplest case when the wave function of an impurity is isotropic (Sec. 2). In Sec. 3 we shall generalize this theory to the case of anisotropic wave functions and discuss the influence of pressure on the resistivity ρ_3 . In Sec. 4 we shall consider the hopping conduction in strong magnetic fields. Sections 5 and 6 are devoted to the activation energy ε_3 in the case of weak and strong compensation. Finally, Sec. 7 deals with the hopping conduction at very low temperatures, when Eq. (1) is no longer valid and σ decreases in accordance with the law $\exp\{-(T_0/T)^{1/4}\}$, which was predicted by Mott [5].

2. RESISTIVITY ρ_3 FOR ISOTROPIC IMPURITY STATES

We shall at first assume that the temperature is so high that there are sufficient phonons for electron jumps. Then, the probability of a jump W_{ij} depends weakly on T and is given by Eq. (3). It follows from Eq. (1) that we can find ρ_3 by calculating the hopping resistivity at high temperatures. Miller and Abrahams [13] have shown that the resistivity ρ_3 can be calculated using an equivalent circuit, which is a three-dimensional network of resistances in which each joint represents a definite donor and the resistance between any two donors i and j is proportional to W_{ij}^{-1} , i.e., it is proportional to $e^{2r_{ij}/a}$. We shall calculate the resistance of such a random network by the method suggested in [8]. We shall then show that the method employed by Miller and Abrahams leads to incorrect results.

We shall consider all possible chains of donors joining two opposite surfaces of a crystal (contacts). In each chain the resistances are connected in series and, therefore, the resistance of a chain is governed by the elements with the largest values of r_{ij} . We shall represent each chain by R , which is the maximum size of the elements in it. If there are many chains, those with lower values of R shunt the chains with higher values of R and govern the resistance of the whole network. Thus, the most important are the chains with the lowest values of R . One might assume that there is no lower limit to the value of R for any given chain. In a random distribution of impurities there is a very small but finite probability that two donors will be separated by a very short distance and that the third, fourth, etc., donors will approach very closely the original pair. However, if $R \ll N_D^{-1/3}$, this probability decreases very rapidly with increasing length of the chain because it is proportional to $(N_D R^3)^m$, where m is the number of links in the chain. We are interested in the formation of an infinite chain ($m \rightarrow \infty$). In this case, the probability of very close spacing of all the donors in a chain vanishes for $R \ll N_D^{-1/3}$. Thus, a network will not have any chains which connect opposite faces of the sample and which are characterized by $R \ll N_D^{-1/3}$.

On the other hand, it is self-evident that there will be a very large number of chains with $R \gg N_D^{-1/3}$. Hence, it follows that there is a critical value $R = R_C$, beginning from which chains joining both contacts will appear in an infinite crystal. Moreover, it is clear that R_C is close to the average distance between donors $N_D^{-1/3}$. In other words, the volume of a sphere of radius R_C is of the or-

der of the average volume occupied by a donor (N_D^{-1}), i.e.,

$$\frac{4\pi}{3} N_D R_C^3 = \beta_0, \quad (4)$$

where β_0 is a coefficient of the order of unity. It is not possible to calculate β_0 analytically. The mathematical task of finding β_0 has been considered in [14] in connection with a different physical problem. The value of β_0 was found in that paper by the Monte Carlo method with the aid of a computer. It was found that $\beta_0 = 2.32$, i.e., $R_C = 0.82 N_D^{-1/3}$. The calculations reported in [14] confirmed that there should be no chains with $R < R_C$. Moreover, they showed that a considerable fraction of all the donors should be localized in chains with R exceeding R_C only by 10–15% ($R \approx 0.9 N_D^{-1/3}$). Since the resistance of a chain with a specified value of R is proportional to $e^{2R/a}$ and since it increases rapidly with R , it follows that the resistance of the whole crystal is governed by the chains for which R is only slightly higher than R_C , i.e., we find that

$$\rho_3 = \rho_0 e^{f(N_D)}, \quad f(N_D) = \frac{a}{N_D^{1/3} a}, \quad (5)$$

where a is about 10% larger than $2(3\beta_0/4\pi)^{1/3} = 1.64$, i.e., it is close to 1.8.

The mathematical task of calculating R_C , i.e., the task of finding ρ_3 , can be formulated in the language used to deal with the percolation of a liquid in a random maze of channels [15]. We shall assume that a "wet" donor can "wet" a neighboring donor only if the separation between them is less than R . Then, R_C is that value of R for which one "wet" donor can "wet" an infinite number of other donors (the donor concentration N_D is assumed to be fixed). Therefore, the method we shall use to find ρ_3 can be called the percolation method.

We thus obtain $f(N_D)$ for hydrogen-like impurity states. However, the percolation method cannot be used to find the preexponential factor ρ_0 in spite of the fact that the coefficient in the equation for the probability of a jump (3) can be calculated quite rigorously [13]. The difficulty arises because we do not know the exact number of chains which make the main contribution to ρ_3 (i.e., the chains with $R \geq R_C$) and the number of links in each of these chains. We can only say that these quantities depend, in a power-law manner, on the value of N_D , so that the resistivity ρ_0 is also a power function of N_D . Since the resistivity ρ_0 does not contain any large parameter, its order

of magnitude should be the same as that of the "band" resistivity of N_D electrons, i.e., it should be of the same order as ρ_1 . This is indeed observed experimentally.

Miller and Abrahams [13] calculated the resistivity ρ_3 of a random network by a more complex and very artificial method. We shall give a simple interpretation of their calculation and try to find the physical origin of the errors they committed. Miller and Abrahams [13] assumed that because of a random distribution of impurities in a crystal there are regions of radius r greater than $N_D^{-1/3}$ in which there are no donors. The probability of the appearance of a depletion region r^3 is given by the Poisson distribution [16] and is equal to $\exp(-N_D r^3)$. Next, Miller and Abrahams assumed effectively that any chain of donors connecting two contacts intersects such regions. An electron jump across a region of this kind is highly unlikely, i.e., a donor-depleted region has a very high resistance, of the order of $\exp(r/a)$. The contribution of the donor-depleted regions of radius r to the resistance of a chain is proportional to

$$\exp\left(\frac{r}{a}\right) \exp(-N_D r^3). \quad (6)$$

The product (6) has a sharp peak at the point where R is of the order of $(aN_D)^{-1/2} \equiv R_m$. Since all the resistances in a chain are connected in series, the total resistance of the chain is dominated by the elements of length close to R_m . We shall find the resistance of a chain of this kind by substituting R_m in Eq. (6). If we assume that all the chains have the same resistances, we find that the resistivity of a crystal is given by

$$\rho_3 \propto \exp\left\{ (N_D a^3)^{-1/2} \right\}. \quad (7)$$

The above expression is the main result of Miller and Abrahams (we deliberately omitted the numerical coefficients in the argument of the exponential function). We can see that the resistivity found by the percolation method [Eq. (5)] for a lightly doped ($N_D^{-1/3} \gg a$) semiconductor is much smaller than the resistivity given by Eq. (7). The reason why Miller and Abrahams obtained an overestimated value is quite clear. Obviously, in addition to the chains which intersect donor-depleted regions, there must be a very large number of chains which bypass such regions (Fig. 1). Large donor-depleted regions are very rare and it would not be difficult to imagine a chain which would bypass even large regions. A clear proof of these conclusions

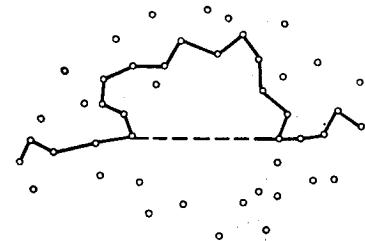


Fig. 1. Circles denote donors and the solid line is a low-resistance chain bypassing all the random donor-depletion regions. The dashed line represents the intersection of a donor-depletion region, as postulated by Miller and Abrahams [13].

is provided by the computer calculations reported in [14]. The chains which bypass the donor-depleted regions shunt the chains with higher resistances and reduce the resistivity of the whole crystal to the value given by Eq. (5).

The result given by Eq. (5) differs also considerably from the equation

$$f(N_D) = \frac{0.9}{N_D^{1/3} a}, \quad (8)$$

which was obtained by Mott and Twose [1] with the aid of an approximate method for the averaging of the resistances of chains suggested by Pippard. We shall show later that the experimental data support Eq. (5).

The fullest information on the dependence of the hopping conductivity on the concentration of the principal impurities is available for n- and p-type germanium [17, 18]. However, the theory we have employed so far is applicable only to isotropic wave functions of impurities. Therefore, strictly speaking, it cannot be applied to germanium because the wave functions of the impurities in this semiconductor are anisotropic. Nevertheless, we can compare Eq. (5) with the data for p-type germanium. This is because the overlap integral of Eq. (2) is dominated by the asymptotic behavior of the wave function at large distances from an impurity. In the case of acceptors, this behavior is governed by the light holes [19]. Since the ridge in the constant-energy surface of the light holes does not exceed 6% [20], it can be ignored in the first approximation to the problem. Then, the wave function of an acceptor at large distances from it is of the form [19]

$$\psi_i(r) \propto e^{-\frac{|r-r_i|}{a_l}}, \quad a_l = \frac{\hbar}{\sqrt{2m_l^* E}}, \quad m_l^* = 0.047 m. \quad (9)$$

Here, E is the ionization energy of the acceptor; m_l^* is the effective mass of the light holes; m is

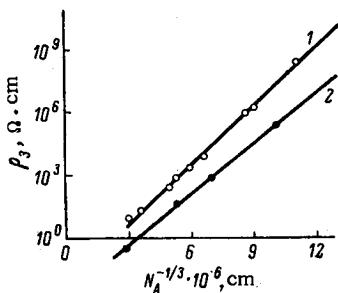


Fig. 2. Dependence of the resistivity ρ_3 of gallium-doped germanium on the concentration of gallium: 1) undeformed crystal; 2) crystal subjected to uniaxial pressure. The degree of compensation of all the samples was $K = 0.4$.

the mass of free electrons. Fritzsche and Cuevas [18] studied germanium in which the principal impurity was gallium and for which the degree of compensation was 0.4. In this case, $E = 10.8$ meV and $a_l = 87$ Å, so that Eq. (5) leads to $f_{\text{theor}}(N_A) = 1.15\alpha \cdot 10^6 \text{ cm}^{-1} \cdot N_A^{-1/3}$ (the concentration N_A is used instead of N_D because we are now talking of a p-type semiconductor). The experimentally determined value of $\log \rho_3$ is found by extrapolation of the dependence of $\log \rho$ ($1/T$) to infinite temperatures. Points denoted by 1 in Fig. 2 represent the dependence of $\log \rho_3$ on $N_A^{-1/3}$ taken from [18]. We can see that this dependence is linear and that the slope of the line gives $f_{\text{exp}}(N_A) = (2.2 \pm 0.1) \cdot 10^6 \text{ cm}^{-1} \cdot N_A^{-1/3}$. Comparing $f_{\text{exp}}(N_A)$ with $f_{\text{theor}}(N_A)$, we find that $\alpha = 1.9 \pm 0.1$. This value of α is in satisfactory agreement with the theoretically predicted $\alpha = 1.8$.

Fritzsche and Cuevas [18] analyzed their results using the equation of Mott and Twose (8) and found that $\alpha = 40$ Å for gallium. They remarked on the good agreement between this value and those obtained from the hydrogen-like model and the variational calculations of the acceptor states [21]. However, we have already pointed out that the Bohr radius, which describes the asymptotic behavior of a wave function, is completely unrelated to these values. If we use the correct radius $\alpha = a_l = 87$ Å, we find that the equation of Mott and Twose for $f(N_A)$ diverges by a factor of more than 2 from the experimental data.

The ridge in the constant-energy surface of the light holes in silicon does not exceed 12% and, therefore, Eq. (5) can be compared with the results on the hopping conductivity of weakly compensated p-type silicon [22]. Figure 3 shows the dependence of $\log \rho_3$ on $N_A^{-1/3}$ for boron-doped silicon. We can see that this dependence is nearly linear. The slope gives $f_{\text{exp}}(N_A) = 8.6 \cdot 10^{-6} \text{ cm}^{-1}$.

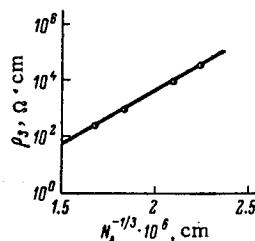


Fig. 3. Dependence of the resistivity ρ_3 of boron-doped silicon on the concentration of boron.

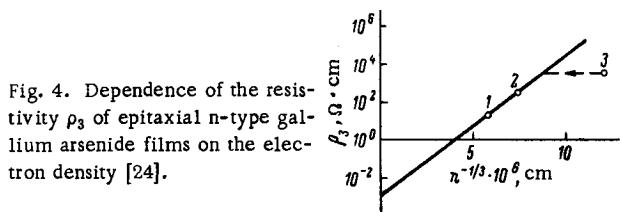


Fig. 4. Dependence of the resistivity ρ_3 of epitaxial n-type gallium arsenide films on the electron density [24].

$N_A^{-1/3}$. If the average mass of the light holes is taken to be $m_l^* = m/6$ [20] and the ionization energy of boron is assumed to be $E = 45$ meV [23], we find that $a_l = 22.8$ Å. The substitution of a_l into Eq. (5) gives $f_{\text{theor}}(N_A) = 4.4\alpha \cdot 10^{-6} \text{ cm}^{-1} \cdot N_A^{-1/3}$ and a comparison of f_{theor} with f_{exp} yields $\alpha = 1.9$. This value is in agreement with that obtained for gallium-doped germanium and is close to the theoretical value of 1.8. However, it should be pointed out that whereas in gallium-doped germanium α is obtained to within 5%, in the case of silicon the same parameter α is found to within 10–15%.

We shall not analyze the data on gallium- and aluminum-doped silicon [22] because of the correlation observed in the distribution of impurities in these materials.

The good agreement between the theory and the experimental data can be regarded as a confirmation of the theory of hopping conduction based on the percolation method. One can also assume that the method is correct and regard the agreement with the experimental results as a confirmation of the correctness of our calculations of the Bohr radii. In those cases when the Bohr radius is unknown, it can be found by analyzing the dependence of $\log \rho_3$ on $N_D^{-1/3}$ on the assumption that $\alpha = 1.8-1.9$.

It is difficult to compare the theory with the data on AIIIBV crystals because, usually, the concentration of the principal impurity is not known sufficiently accurately for samples with the very lowest carrier densities. However, we shall show that, in this case, Eq. (5) can be used to obtain some additional information. We shall do this by considering the data reported in [24] on the hopping

conduction in epitaxial films of n-type gallium arsenide (Fig. 4). Equation (5) is applicable to gallium arsenide because the wave functions of electrons localized at donors are isotropic. If we use $m^* = 0.07m$ and $E = 5.7$ meV, we find that $a = 97 \text{ \AA}$. If we assume that $\alpha = 1.8$, we find that Eq. (5) yields $f_{\text{theor}}(N_D) = 1.75 \cdot 10^6 \text{ cm}^{-1} \cdot N_D^{-1/3}$. Figure 4 shows the dependence of $\log \rho_3$ on the average distance between electrons ($n^{-1/3}$). Let us see what we shall find if we assume that $N_D = n$. Let us draw a straight line with a slope given by the expression for $f_{\text{theor}}(N_D)$ in such a way that it passes through the point 1. We find that the same line also passes through the point 2 (Fig. 4) and that the intercept on the ordinate gives the usual value $\log \rho_0 \approx -3$. Consequently, the assumption that $n = N_D$ leads to good agreement between the theory and experimental data for samples 1 and 2. Hence, we may conclude that the compensation of these samples is weak. The point denoted by 3 is outside the theoretical line and, therefore, it is not permissible to assume that $n = N_D$ in sample 3. If we shift point 3 so that it falls on the line, we can estimate the impurity concentration in sample 3. Such an estimate gives $N_D/n \approx 2.7$ ($K \approx N_A/N_D \approx 0.63$). Thus, the degree of compensation can be calculated approximately with the aid of Eq. (5).

3. RESISTIVITY ρ_3 FOR ANISOTROPIC IMPURITY STATES

The assumption that at large distances the wave function of an electron attached to an impurity decreases isotropically in accordance with the law $\exp(-r/a)$ restricts strongly the range of applications of the theory proposed in Sec. 2. For example, this theory cannot be applied to n-type germanium or n-type silicon because the wave functions of donors in these materials are strongly anisotropic. Moreover, the isotropic form of the theory cannot be applied to hopping conduction in strong magnetic fields because, in this case, the wave functions of impurities are strongly elongated along the field. In this section, we shall generalize the theory to the case of anisotropic wave functions and then compare the results obtained with the experimental data on n-type germanium.

If the wave functions of impurities i and j are anisotropic, the overlap integral (2) and the jump probability W_{ij} depend not only on the distance between impurities, but also on the orientation of the vector \mathbf{r}_{ij} joining these two impurities with respect to the crystallographic axes or to the applied magnetic field. We shall consider first the i -th impurity and construct around it a constant-over-

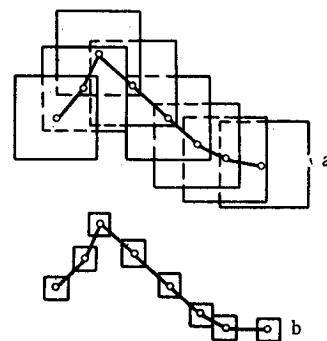


Fig. 5. Circles represent donors and squares around each donor are the anisotropic "surfaces" S_L . In the upper half of the figure the squares correspond to larger values of L than in the lower half. We can see that percolation along the same chain may occur at large values of L but not at low values of this parameter.

lap surface S_L in accordance with the equation

$$-\ln W_{ij}(\mathbf{r}_{ij}) = L, \quad L \gg 1. \quad (10)$$

This surface is the geometrical locus of the positions of the impurity j for which the probability of a jump from the central impurity (i) is constant and given by Eq. (10). For convenience, we are using the minus sign in Eq. (10) and replacing W_{ij} with $\ln W_{ij}$ because the probability W_{ij} is exponentially small. The dimensions of the surface S_L increase with increasing L . This follows from an analysis of the case of an isotropic wave function when W_{ij} is given by Eq. (3), and Eq. (10) is of the form $2|\mathbf{r}_{ij}|/a = L$ and defines a sphere of radius $aL/2$. The same example also shows that if \mathbf{r}_{ij} lies inside the surface S_L , the probability W_{ij} is greater than e^{-L} .

We shall assume that surfaces S_L corresponding to the same value of L are constructed around every impurity on the assumption that every impurity is located at the center of a coordinate system. It follows that in a chain of impurities in which each donor lies inside the surface S_L of the preceding donor (Fig. 5a), the exponential factor in the resistance of such a chain does not exceed e^L . The question now arises as to what is the smallest value of L for which we can have an infinite chain of the type shown in Fig. 5a. If L is so small that the volume $V(L)$ enclosed by the surface S_L is small compared with the average volume occupied by one donor (N_D^{-1}), we cannot find an infinite chain which will satisfy the stated condition. At low values of L the surface S_L only rarely contains two donors. In other words, there is no percolation for these values of L (Fig. 5b). If

L is so large that $V(L) \gg N_D^{-1}$, the number of chains joining both contacts is very large. Therefore, there must exist a critical value L_C of the constant L which is a measure of the size of the surface S_L and at which infinite chains appear first, i.e., the value corresponding to the onset of percolation. Clearly, the value of L_C is defined by the condition

$$V(L_C) N_D = \beta_S, \quad (11)$$

where β_S is a numerical coefficient of the order of unity, and usually depends on the shape of the surface S_L . If we adopt the percolation approach, we may assume that when L exceeds by 10–15% the value L_C the number of infinite chains will be large. If the coefficient β_S is found by numerical calculations and L_C is deduced from Eq. (11), we find that

$$\rho_3 \propto e^{f(N_D)}, \quad (12)$$

where $f(N_D)$ is only several percent larger than L_C .

We shall now consider a general method for finding ρ_3 by analyzing the isotropic case mentioned above. In this case, S_L is a sphere of radius $aL/2$ and the parameter β_S is known and equal to $\beta_0 = 2.32$ [see Eq. (4)]. Therefore, $V(L) = \pi a^3 L^3 / 6$ and $L_C = 1.64 N_D^{-1/3} a$, i.e., we again obtain the result given by Eq. (5).

We shall now apply the general equation (12) to n-type germanium. It is known [23] that the wave function of an electron localized on a donor is of the form

$$\psi_i(\mathbf{r}) = \sum_{n=1}^4 C_n F_n(\mathbf{r}) \Phi_n(\mathbf{r}), \quad (13)$$

where $\Phi_n(\mathbf{r})$ is the Bloch function for the n -th valley in the conduction band and $F_n(\mathbf{r})$ is the slowly varying envelope function. Usually, the latter is written in the form

$$F_n(\mathbf{r}) = (\pi a^2 b)^{-1/2} \exp \left\{ - \left[\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2} \right]^{1/2} \right\}, \quad (14)$$

where the z axis is parallel to the directions of the [111] type, along which the n -th valley is oriented. The semiaxes of the ellipsoid (a and b) are found by variational calculations. However, we can show that at large distances from a donor the exact solution of the Schrödinger equation has an exponential factor of the type given by Eq. (14) and the parameters a and b are then defined by [13]

$$a = \frac{\hbar}{\sqrt{2m_{\perp}^* E}}, \quad b = \frac{\hbar}{\sqrt{2m_{\parallel}^* E}}, \quad (15)$$

where $m_{\perp}^* = 0.082m$, $m_{\parallel}^* = 1.56m$, and E is the binding energy of the donor. Calculation of the probability of a jump, carried out making an allowance for the orthogonality of the Bloch functions of the various valleys, gives [13]

$$W_{ij} \simeq \sum_{n=1}^4 e^{-\frac{2R_n}{a}}, \quad (16)$$

where

$$R_n = a \left(\frac{x_{ij}^2 + y_{ij}^2}{a^2} + \frac{z_{ij}^2}{b^2} \right)^{1/2}, \quad x_{ij} = x_i - x_j.$$

According to the definition (10), the surface S_L is now the envelope of four intersecting oblate ellipsoids oriented along the [111] axis. Each ellipsoid is given by the equation

$$2 \left(\frac{x^2}{a^2} + \frac{z^2}{b^2} \right)^{1/2} = L. \quad (17)$$

Unfortunately, the coefficient β_S for such a complex surface is not known and the numerical value of the factor in the function $f(N_D)$ cannot be found theoretically. Nevertheless, we can say that because the semiaxes of each ellipsoid of Eq. (17) are $aL/2$, $bL/2$, and the volume is $(L/2)^3 4\pi a^2 b/3$, it follows that $V(L) \propto L^3 a^2 b$. If we find L_C from Eq. (11), we then obtain

$$f(N_D) \propto \frac{1}{N_D^{1/3} (a^2 b)^{1/3}} \propto \frac{E^{1/2}}{N_D^{1/3}}. \quad (18)$$

Let us compare this result with the experimental data. Figure 6 shows the dependence of ρ_3 on T^{-1} for n-type germanium doped with antimony [17]

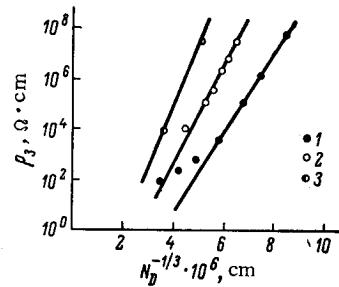


Fig. 6. Dependence of the resistivity ρ_3 on the average distance between donors $N_D^{-1/3}$: 1) antimony-doped germanium [17]; 2) phosphorus-doped germanium [12]; 3) antimony-doped germanium at maximal pressure [12].

and phosphorus [12]. We can see that at low values of N_D , when the conduction is of hopping nature, the value of $\log \rho_3$ is a linear function of $N_D^{-1/3}$, in agreement with the theory. The slopes of the lines in Fig. 6 differ by a factor of 1.19. According to the theory, this difference should be equal to the square root of the ratio of the ionization energies of phosphorus and antimony. This root is 1.15, so that the agreement between the theoretical and experimental values can be regarded as satisfactory. It is also reasonable to find that the values of $\log \rho_0$ for the two materials are similar to each other and to the value of $\log \rho_1$, which, in this case, is -3 [17].

More definite conclusions can be drawn from the theory in the case of hopping conduction in antimony-doped germanium subjected to a strong uniaxial pressure along the [111] axis. Such compression reduces the energy of one valley in the conduction band and raises the energy of the other three [25]. At pressures of the order of 10^9 dyn/cm² the splitting between the valleys is so large that the ground state of a donor electron is associated not with four ellipsoids (which is the case at atmospheric pressure), but with one ellipsoid. Pressures in excess of 10^9 dyn/cm² do not lead to further significant changes in the wave function. Therefore, the pressure of $\sim 10^9$ dyn/cm² can be regarded as the limiting or "maximal." At "maximal" pressure we are left only with one term in Eq. (13) and, therefore, also in Eq. (16). This term represents an ellipsoid whose axis coincides with the direction of pressure. In this case, the surface S_L is an ellipsoid defined by Eq. (17) and $V(L) = \pi a^2 b L^3 / 6$. It is proved in [10] that the coefficient β_S for an ellipsoidal surface S_L is exactly equal to the coefficient β_S for a sphere, i.e., it is given by $\beta_0 = 2.32$. We can find L_C by applying Eq. (11). This gives

$$\frac{\pi}{6} a^2 b L_C^3 N_D = 2.32, \quad L_C = \frac{1.64}{N_D^{1/3} (a^2 b)^{1/3}}. \quad (19)$$

Finally, we obtain the following expression for ρ_3 :

$$\rho_3 = \rho_0 e^{f(N_D)}, \quad f(N_D) = \frac{\alpha}{N_D^{1/3} (a^2 b)^{1/3}}, \quad (20)$$

where α is the same quantity as in Eq. (5).

In deriving Eq. (20) we have not specified the direction of the current with respect to the compression axis [111]. Clearly, the principal exponential term in the resistivity ρ_0 obtained by the percolation method is completely independent of the direction. If $L \geq L_C$, there may exist chains which penetrate a crystal along all directions. All

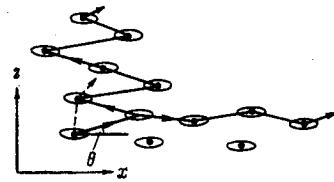


Fig. 7. Ellipses represent the constant-wave-function surfaces constructed around randomly distributed donors. The z axis is the direction of compression [111]. The wave function decreases faster along this axis than along the others. The continuous lines represent the jumps of an electron, which determine the resistivity along the z and x axes; the dashed line is the path of the "head-on" motion along the z axis, for which the resistivity is much higher.

these chains have a resistance proportional to $\exp(L_C)$.

If we do not use the percolation method, we find that at first sight our conclusion on the isotropy of the exponential term is paradoxical. The wave function of a donor at "maximal" pressure is in the shape of an ellipsoid of revolution, which is given by Eq. (14) and is strongly flattened along the [111] axis [the ratio of the semiaxes is $a/b = (m_{||}^*/m_{\perp}^*)^{1/2} = 4.35$]. It would be natural to assume that conduction along any direction is due to electron jumps along this direction. The probability of jumps over the same distance differs exponentially along the [111] axis and at right angles to this axis. Therefore, we would expect the resistivity to be anisotropic and the anisotropy should be so strong that the ratio of the values of ρ_0 along and at right angles to the compression axis is exponentially large. This point of view is reflected, for example, in [25]. However, if we examine carefully Fig. 7, which shows the wave functions of randomly distributed donors which are strongly elongated along the x axis (the z axis corresponds to the direction of compression), we find that, in the case of a fixed donor, the nearest neighbor located in a narrow range of angles from $-\theta$ to θ on the (x, y) surface is far away. Consequently, the current along the x axis is basically due to jumps oriented at finite but small angles θ . The probability of such jumps is exponentially higher than the probability of jumps at angles θ comparable with $\pi/2$. Therefore, an electron moving along the z axis is most likely to travel by way of the most probable jumps, which are the same as those for the x axis (Fig. 7). The principal exponential term $e^{f(N_D)}$ in the resistivity along the x and z directions is the same. The resistivity ρ_z along the z axis is slightly higher than ρ_x because the projection of a typical jump onto the z axis is less than onto the x axis and more jumps

are necessary to travel a unit length along the z axis than along the x axis. However, this is reflected only in the preexponential factor ρ_0 .

The percolation method can be used to show that a typical value of the angle θ is b/a . In fact, the resistivity is governed by jumps characterized by L , which is close to L_C . For these jumps the vector r_{ij} lies on the surface S_{LC} . Since S_{LC} is an ellipsoid with the semiaxes ratio b/a , a typical angle θ is equal to b/a . Thus, we may expect that $\rho_z/\rho_x \approx a/b$, i.e., that the resistivities along the compression axis and at right angles to it differ by a factor of 4-5.

An investigation of the extrinsic conduction in germanium subjected to "maximal" compression along the [111] axis was reported in [25]. However, Fritzsch [25] investigated only samples with fairly high impurity concentrations, close to the critical concentration for the Mott transition. Our theory is applicable to low impurity concentrations when the overlap of the wave functions is exponentially small. Experiments carried out on samples with lower impurity concentrations ($N_D = 2.2 \cdot 10^{16}$ and $6.5 \cdot 10^{15} \text{ cm}^{-3}$) were described in [12]. At the "maximal" pressure the resistivity ρ_3 for the first of these samples rose by a factor of 30 above the atmospheric pressure value, whereas the resistivity of the second sample increased by a factor of 10^4 ! This piezoresistance can justifiably be called a giant effect. The values of ρ_3 obtained in this investigation are plotted in Fig. 6. The slope of the line drawn through two points allows us to check Eq. (20). This line intersects the ordinate at approximately the same place as the other two lines in Fig. 6, which is in agreement with the assumption of a weak dependence of $\log \rho_0$ on the nature of the wave functions of impurities. This can be regarded as evidence that the slope of the straight line drawn through two points is correct. The ionization energy of antimony in germanium is $E = 9.6 \text{ meV}$ and, consequently, we find that

$$a = 71, \quad b = 16, \quad (a^2 b)^{1/3} = 43 \text{ \AA}. \quad (21)$$

If we use these values and measure the slope of the straight line in Fig. 6, we find that the value of α which occurs in Eq. (20) is 1.9. This is in good agreement with the theoretical values and the values of α found in our analysis of the data on p-type silicon and p-type germanium.

The resistivity in [12, 25] was measured along the compression axis. It would be interesting to measure the resistivity in the transverse direction

in order to check the theoretically predicted approximate isotropy of the giant piezoresistance.

In the preceding paragraphs we have considered the influence of uniaxial compression on n-type germanium. Let us now see what the percolation method predicts for p-type germanium.¹

We know that uniaxial compression lifts the degeneracy of the valence band at the point $k = 0$. If the compression along the [100] axis is sufficiently strong, the wave function is of the form given by Eq. (14), where the values of a and b for gallium are 84 and 132 Å and the z axis is parallel to the direction of compression [26, 27]. In this case, we can apply the theoretical equation (20), which differs from Eq. (5) by the introduction of the effective Bohr radius $(a^2 b)^{1/3}$. In the case of gallium, this radius is 98 Å and it is larger than the Bohr radius of gallium $a_l = 87 \text{ \AA}$ for an undeformed crystal (in such a crystal the wave functions are approximately isotropic). Therefore, in contrast to the situation in n-type germanium, uniaxial compression of p-type germanium along the [100] axis does not increase but reduces the resistivity.

The hopping conduction in p-type germanium subjected to pressure along the [100] axis has been investigated by Pollak [27]. The values of ρ_3 extrapolated to infinite pressures are plotted in Fig. 2 (they are denoted by 2). The slope of the line drawn through these points can be used to find α . If we apply Eq. (20), we find that $\alpha = 1.7-1.8$, which is again in satisfactory agreement with the theory and with the experimental values reported in the preceding sections.

4. INFLUENCE OF STRONG MAGNETIC FIELDS ON HOPPING CONDUCTION

The percolation method can be applied also to the problem of hopping conduction in a very strong magnetic field [9]. Such a field compresses the wave functions of impurities and reduces strongly their overlap. For this reason the hopping resistivity increases exponentially in sufficiently strong magnetic fields.

A rise of the hopping resistivity by a factor of 10^5 was reported by Halbo and Sladek [28], who investigated n-type GaAs with donor concentrations $N_D \approx 10^{16} \text{ cm}^{-3}$. The giant positive magnetoresistance was observed earlier by Sladek [29] for n-type InSb with $N_D \approx 5 \cdot 10^{15} \text{ cm}^{-3}$. At these donor concentrations the impurity band overlaps the conduction

¹The author is grateful to G. E. Plikus and G. L. Bir for drawing his attention to the possibility of applying the percolation method to p-type germanium.

tion band if there is no magnetic field, and in such cases the conduction is metallic. However, a magnetic field reduces the overlap of the wave functions of impurities, the impurity band splits off from the conduction band, and the hopping conduction predominates at temperatures below 2°K. Further increase in the magnetic field intensity results in an exponential rise of the hopping resistivity, which can increase by a factor as large as 10^5 . This exponentially large positive magnetoresistance has also been observed in the hopping conduction region of n-type germanium [30], n-type indium phosphide [31], and in gallium arsenide [32, 33] purer than that used in [28].

The application of a magnetic field compresses wave functions and, generally speaking, increases both ρ_3 and ε_3 . In this section we shall consider only the change in ρ_3 . The magnetic-field dependence of ε_3 will be considered in the next section.

An approximate theory of magnetoresistance in moderate magnetic fields was developed by Mikoshiba [34]. If the applied magnetic field is not too strong, the probability of a jump between two hydrogen-like donors along the field (z axis) is still given by Eq. (3). However, if the distance between the donors satisfies the conditions

$$\frac{\lambda^2}{a} \gg r_{ij} \gg a, \quad (22)$$

Mikoshiba [34] finds that the probability of a jump in the transverse direction $r_{ij} \perp H$ is (for details see Appendix)

$$W_{ij} \propto e^{-\frac{2r_{ij}}{a}} e^{-\frac{1}{12} \frac{a r_{ij}^3}{\lambda^4}} (r_{ij} \perp H). \quad (23)$$

Here $a = \hbar/(2m^*E)^{1/2} = \hbar^2\mu/m^*e^2$ is the Bohr radius, $\lambda = (c\hbar/eH)^{1/2}$ is the magnetic length, and μ is the permittivity. If the magnetic field is not too strong and the semiconductor is lightly doped, i.e., if

$$\lambda > \frac{a}{(N_D a^3)^{1/6}} \text{ and } N_D a^3 \ll 1, \quad (24)$$

the conditions given by Eq. (23) are satisfied for moderate distances between the impurities. Although the probability of a jump is anisotropic, the percolation paths are not yet affected by the magnetic field.²

This can be shown by considering a donor 1, whose nearest neighbor 2 is located at a distance r_{12} along the x axis and whose second-nearest neighbor 3 is located at a distance r_{13} ($r_{13} > r_{12}$)

along the z axis. In the absence of a magnetic field the probability of the W_{12} jump is much higher than that of the W_{13} jump and the chain which reaches donor 1 is propagated by the jump $1 \rightarrow 2$. It follows from Eqs. (23) and (3) that the ratio of the jump probabilities in a magnetic field is

$$\frac{W_{12}}{W_{13}} = e^{-\frac{1}{12} \frac{a r_{12}^3}{\lambda^4}} e^{\frac{2(r_{13}-r_{12})}{a}}. \quad (25)$$

The distances r_{12} and r_{13} and the difference between them $r_{13} - r_{12}$ are generally quantities of the order of $N_D^{-1/3}$. Therefore, it is evident from Eq. (25) that when the magnetic field satisfies Eq. (24), we still have $W_{12} \gg W_{13}$ and the percolation chain continues to propagate in the same manner as in the absence of the field. This means that, as in zero field, the jumps in the chains which determine the resistance are almost equally likely along all directions. In particular, such chains have considerable numbers of elements inclined at large angles with respect to the z axis and characterized by the length $r \approx 0.9N_D^{1/3}$. According to Eq. (23), the resistance of these elements increases in a magnetic field by a factor $\exp(0.06 a/\lambda^4 N_D)$. The resistance of the chains and of the whole crystal increases in the same ratio. Thus, the refined result of Mikoshiba [34] is of the form

$$\begin{aligned} \rho_3(H) &= \rho_3|_{H=0} \exp\left\{0.06 \frac{a}{\lambda^4 N_D}\right\} \\ &= \rho_3|_{H=0} \exp\left\{0.06 \frac{a H^2 e^2}{N_D c^2 \hbar^2}\right\}. \end{aligned} \quad (26)$$

The present author [9] derived the dependence $\rho_3(H)$ for stronger magnetic fields which do not satisfy the conditions of Eq. (24) for which Eq. (26) is invalid. These fields can be established quite easily in semiconductors with small effective masses. If $\lambda < a/(N_D a^3)^{1/6}$, the argument in the exponential term of the wave function of a donor is affected strongly by a magnetic field at distances of the order of $N_D^{-1/3}$. In particular, if $\lambda < a$, the ionization energy of a donor $E(H)$ increases with increasing H and the wave function is of the form [35-37]

$$\psi_i(r) = B \exp\left\{-\frac{x^2 + y^2}{4\lambda^2} - \frac{|z|}{a_H}\right\}. \quad (27)$$

²In the percolation method we employ not the probability of a jump, but its logarithm. It follows from Eqs. (3), (23), and (24) that the anisotropy of $\ln W_{ij}$ is small at distances $r_{ij} \approx N_D^{-1/3}$. Therefore, the surface S_L is nearly spherical and the percolation paths are modified only very slightly by the magnetic field.

Here, $a_H = \hbar/(2m^*E(H))^{1/2}$, the z axis is directed along H, and B is a normalization constant. If $a < \lambda < a/(Na^3)^{1/6}$, the magnetic field affects only slightly the wave function near an impurity center, but at distances of the order of $N_D^{-1/3}$ the changes are large and the wave function is again of the type given by Eq. (27) [9] (for details see Appendix). Calculation of the overlap integral of two wave functions of the type given by Eq. (27) yields

$$W(r_{ij}) = \exp \left\{ -\frac{x_{ij}^2 + y_{ij}^2}{2\lambda^2} - \frac{2|z_{ij}|}{a_H} \right\}, \quad (28)$$

where $x_{ij} = x_i - x_j$. We can easily show that in strong fields ($\lambda < a/(Na^3)^{1/6}$) the anisotropy of the probability of a jump given by Eq. (28) is so strong that, in the case of three donors mentioned above, we find that, in spite of the fact that $r_{13} > r_{12}$, the jump $1 \rightarrow 3$ is much more likely because it is aligned along the magnetic field. This means that a strong magnetic field modifies greatly the percolation paths so that a large number of jumps occur at small angles with respect to the field direction (this situation is illustrated in Fig. 7 if it is assumed that the field is applied along the x axis).

Sladek [29] calculated ρ_3 in strong magnetic fields with the aid of the variational wave function [38]

$$\psi_i(r) = (2\pi^{3/2}a_{\perp}^2 a_{\parallel})^{-1/2} \exp \left(-\frac{x^2 + y^2}{4a_{\perp}^2} - \frac{z^2}{4a_{\parallel}^2} \right), \quad (29)$$

whose asymptotic behavior at large distances z differs from the behavior predicted by Eq. (27). This difference is very important because jumps occur at small angles with respect to the z axis. Sladek calculated the probability W_{ij} with the aid of the wave function given by Eq. (29) and averaged out the probability over all the (i, j) pairs with fixed distances $|r_{ij}|$. This average is governed by the pairs whose vectors r_{ij} are directed exactly along the z axis. Obviously, the whole crystal cannot be traversed by jumps between these pairs alone and, therefore, the averaging must be carried out not for one isolated pair of donors but for chains penetrating the whole crystal. Thus, the correct results can be obtained only by the percolation method.

We shall find ρ_3 corresponding to $\lambda < a/(Na^3)^{1/6}$ by the percolation method and we shall start by defining the surface S_L which is obtained in the present case. Equations (10) and (28) yield the following expression for S_L :

$$\frac{x^2 + y^2}{2\lambda^2} + \frac{2|z|}{a_H} = L. \quad (30)$$

This surface consists of two paraboloids of revolution, which are in contact along their bases and whose axis is directed along the field H. The height of each paraboloid is $h = aL/2$ and the radius of the base is $d = \lambda\sqrt{2L}$. The volume of such a double paraboloid is given by the expression

$$V(L) = \pi\lambda^2 a L^2. \quad (31)$$

In order to find L_C , we first obtain the following expression from Eqs. (31) and (11):

$$\pi\lambda^2 L_C^2 a N_D = \beta_p, \quad (32)$$

where β_p is the unknown coefficient β for a double paraboloid. Arguments showing that β_p does not differ by more than 10% from $\beta_0 = 2.32$ are given in [9]. Using Eq. (32) to find L_C from Eq. (32) in accordance with the general prescription in Sec. 3, we find that

$$\rho_3(H) = \rho_0 \exp \left\{ [\lambda^2 a_H N_D]^{-1/2} \right\}. \quad (33)$$

When $\lambda \ll a$, the value of a_H is equal to $a \ln^{-1}(a/\lambda)^2$ [35, 36] and, therefore, it follows from Eq. (33) that when $H \rightarrow \infty$, the resistivity $\rho_3(H)$ is proportional to $\exp(-H^{1/2} \ln^{1/2} H)$. When $\lambda \geq a$, we can find a_H from the values of $E(H)$ deduced numerically [36, 38]. We can also substitute in Eq. (33) the values of $E(H)$ found from the Hall effect measurements in that range of temperatures in which the conductivity is governed by activated electron transitions to an allowed band [29]. In all cases, this leads to the dependence $\rho_3(H) \propto \exp(H^m)$, where m is somewhat larger than 0.5. For example, it is shown in [39] that, in the range of fields 20–150 kOe, the theoretical and experimental dependences $E_H(H)$ obtained for InSb can be described satisfactorily by the equation $E_H \propto H^{1/3}$. The application of this equation yields $a_H \propto H^{-1/6}$ and $\rho_3(H) \propto \exp(H^{7/12})$.

In Sec. 3 we have considered experiments involving uniaxial compression of germanium and have shown in detail that, even in the case of strong anisotropy of the wave functions, the principal exponential term in the resistivity ρ_0 is independent of the direction of the current. Thus, Eq. (33) applies to the longitudinal ρ_{\parallel} and the transverse ρ_{\perp} magnetoresistance. The value of ρ_{\perp} should be only several times larger than ρ_{\parallel} . A more accurate estimate of the ratio $\rho_{\perp}/\rho_{\parallel}$ can be obtained by calculating $|z_{ij}/x_{ij}|$ for a typical jump. The radius vectors r_{ij} for a typical jump end on the double

paraboloid of Eq. (30) with $L = L_C$. Consequently, typical values of $|z_{ij}/x_{ij}|$ are close to the ratio of the height of the paraboloid $h(L_C)$ to its radius $d(L_C)$:

$$\frac{|z_{ij}|}{|x_{ij}|} \approx \frac{h(L_C)}{d(L_C)} = 0.4 \left(\frac{a_H}{\lambda} \right)^3 \frac{1}{(N_D a_H^3)^{1/6}}.$$

In the case of samples subjected to the highest magnetic field ($H = 28$ kOe) used in [29], we find that $\lambda = 150$, $a_H = 500$ Å, and $(N_D a_H^3)^{1/6} \approx 1$. If we use these quantities, we find that $|z_{ij}/x_{ij}| = 2.3$. Thus, we can say that, in this case, $\rho_{\perp}/\rho_{\parallel} = 2-3$. This conclusion is in good agreement with the experimental results. Sladek [29] reports that in $H = 28$ kOe the magnetoresistances ρ_{\perp} and ρ_{\parallel} increase by a factor of nearly 10^5 , whereas their ratio $\rho_{\perp}/\rho_{\parallel}$ is still about 2.5 (sample B-1).

We shall now compare the dependences $\rho_3(H)$ given by Eqs. (26) and (33) with the experimental results. The Mikoshiba equation (26) is valid, as stressed in its derivation, at low donor concentrations and in moderately strong fields [see the inequalities in Eq. (24)]. These conditions are satisfied by the most lightly doped samples of germanium, indium phosphide, and indium arsenide investigated by various workers [30-33]. In all these investigations the resistivity ρ increases in a magnetic field in accordance with the law

$$\rho \propto \exp(\text{const } H^2). \quad (34)$$

The activation energy ϵ_3 of the samples with fewest impurities is independent of the magnetic field [30-32] and, therefore, the behavior of ρ predicted by Eq. (34) is entirely due to the increase in ρ_3 . Thus, the results reported in [30-32] are in agreement with Eq. (26).

It is reported in [26, 33] that in magnetic fields $H = 20-30$ kOe the epitaxial films of n-type GaAs with donor concentrations of $(1-5) \cdot 10^{15} \text{ cm}^{-3}$ (these are the same samples as in Fig. 3) exhibit a deviation from the law (34) in the direction of weaker dependence on H . If the value of N_D is reduced, these deviations are observed in weaker fields. Obviously, such deviations can be regarded as the onset of the transition from the law (26) to the law (33). The magnetic field H_0 in which this transition occurs can be estimated roughly from the condition $\lambda \approx a/(Na^3)^{1/6}$. A somewhat more rigorous criterion of the transition from Eq. (26) to Eq. (33) can be obtained by equating Eq. (25) to unity for $r_{12} \approx r_{13} \approx r_{12} - r_{13} \approx N_D^{-1/3}$. This gives

$$\lambda \approx \frac{a}{2(Na^3)^{1/6}} \text{ and } H_0(N_D) \approx \frac{4N_D^{1/2}c\hbar}{ae}. \quad (35)$$

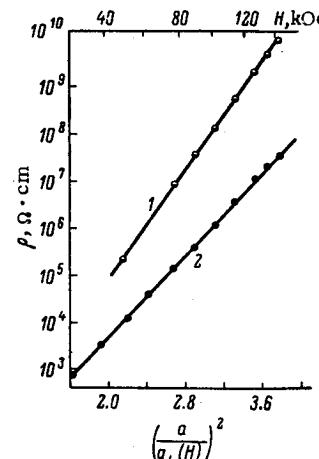


Fig. 8. Dependences of the resistivity of a crystal of n-type GaAs on the quantity $(a/a_{\perp}(H))^2$ and on the magnetic field H (upper scale) [28]. $T(\text{K})$: 1) 1.9; 2) 4.2.

It follows from Eq. (35) that, first, H_0 does indeed decrease with decreasing impurity concentration. Secondly, Eq. (35) gives the correct order of magnitude of H_0 . For example, Eq. (35) predicts $H_0 \approx 25$ kOe for n-type GaAs with $N_D = 10^{15} \text{ cm}^{-3}$.

Halbo and Sladek [28] measured the magnetoresistance of n-type GaAs crystals with donor concentrations $N_D = 10^{16} \text{ cm}^{-3}$. This was done in fields up to 140 kOe. According to Eq. (35), the transition field for these donor concentrations should be $H_0 \approx 50$ kOe so that in a wide range of fields 50 kOe $< H_0 < 140$ kOe the resistivity ρ_3 should obey Eq. (33). The dependence of the resistivity on $(a/a_{\perp}(H))^2$ is plotted in Fig. 8 on the basis of the results reported by Halbo and Sladek [28]. Here, $a_{\perp}(H)$ is the variational parameter describing the transverse dimensions of the wave function given in Eq. (29). It follows from Fig. 2 in [38] that in the range $1.6 < (a/a_{\perp}(H))^2 < 4$ the quantity $(a/a_{\perp}(H))^2$ is proportional to H^m , where $m \approx 0.6$. This can be demonstrated directly with the aid of Fig. 8 by comparing the lower scale of the values of $(a/a_{\perp}(H))^2$ with the upper scale, which gives the magnetic field H . The experimental points in Fig. 8 fit straight lines satisfactorily, which means that in strong fields the resistivity ρ depends on H , in accordance with the law

$$\rho \propto \exp(\text{const } H^m), \quad (36)$$

where $m \approx 0.6$.

In order to compare Eq. (36) with the theoretical equation (33), we must eliminate from Eq. (36) the temperature-dependent parameter $\exp(\epsilon_3(H)/kT)$ and separate $\rho_3(H)$. Since the ratio

$$\frac{\rho(H, T_1)}{\rho(H, T_2)} = \exp \left\{ \epsilon_3(H) \left(\frac{1}{kT_1} - \frac{1}{kT_2} \right) \right\} \quad (T_1 = 1.9, T_2 = 4.2^\circ \text{ K}) \quad (37)$$

depends strongly on H (Fig. 8), it follows that the

dependence $\varepsilon_3(H)$ cannot be ignored under the experimental conditions employed in [28]. On the other hand, since the same dependence $\log \rho \propto H^m$ is obtained at different temperatures, we may conclude [28] that $\rho \propto \exp \{H^m(C_1 + C_2/T)\}$. Thus, we find that $\rho_3(H) \propto \exp(\text{const } H^m)$, where $m \approx 0.6$, which is in good agreement with Eq. (33). The reason why ε_3 increases with increasing field H will be considered in the next section.

In concluding this section, we shall consider the possibility of comparing our theory with the results reported in [27]. We have mentioned that the wave functions of impurities in samples of n-type InSb studied by Pollak [27] overlap strongly, i.e., that $N_D a^3 \approx 1$. Hence, the hopping conduction appears in these samples only when $\lambda < a$, i.e., when the magnetic field reduces considerably the "volume" of each of the impurity wave functions. Thus, in this case, there is no range in which Eq. (26) can be applied, and as soon as the resistivity becomes exponentially large it should obey Eq. (33). An analysis of the results given by Sladek [29] shows that ρ varies in accordance with Eq. (36) and the power exponent m satisfies the inequality $0.7 < m < 0.9$. It is difficult to compare this law with Eq. (33) because it is not possible to determine the value of ρ_3 from the results given in [29]. One can find ρ_3 if the dependence of ρ on $1/T$ is known in a range of temperatures sufficiently wide to enable us to extrapolate to $T \rightarrow \infty$. However, in the case of the results reported in [29], we are dealing with the onset of the hopping conduction even at the lowest temperature of $T = 1.6^\circ\text{K}$. Thus, one can compare Eq. (33) with the data on InSb only for the results obtained at temperatures lower than those employed in [29].

5. ACTIVATION ENERGY ε_3 UNDER WEAK COMPENSATION CONDITIONS

The existence of an activation energy in the case of very weak compensations ($K \ll 1$) has been explained by Mott [1, 40]. If the compensation is weak, a large proportion of donors are occupied by electrons and only a few are vacant. These vacant donor states can be regarded as carriers: A transition of an electron from an occupied to a vacant donor is equivalent to the motion of a positive vacancy in the lattice. At low temperatures all such vacancies are in the states of minimal energy, i.e., they are located in the direct vicinity of the negatively charged acceptors. In other words, electrons occupy all the donors except those whose energy levels are lifted sufficiently high by the nearby acceptors (Fig. 9). Therefore, the Fermi level lies

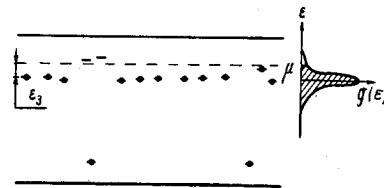


Fig. 9. Energy level scheme of a weakly compensated semiconductor. The continuous lines represent the bottom of the conduction band and the top of the valence band. The black dots are the electrons occupying donor and acceptor levels. The dashed line is the position of the Fermi level. The first acceptor on the left forms a 2-type complex and the second a 0-type complex. The density of donor states is plotted on the right. The occupied states are shown shaded.

above the energy of isolated donors and the gap between them is of the order of the energy of the Coulomb interaction between an acceptor and the nearest donor: $e^2 \kappa^{-1} N_D^{-1/3}$. If $K \ll 1$, the acceptors are separated by large distances and, therefore, a vacancy cannot jump directly from one acceptor to another. In order to travel along a crystal a vacancy must absorb a phonon, become detached from an acceptor, and jump between donors which are separated by large distances from the acceptors. The levels of such donors are shifted very little by the potential of the charged acceptors and donors (Fig. 9) and, therefore, the activation energy is described quite accurately by the difference between the Fermi level and the energy of isolated impurities. This leads to Mott's estimate

$$\varepsilon_3|_{K \rightarrow 0} = C \frac{e^2 N_D^{1/3}}{\kappa}, \quad (38)$$

where C is a numerical coefficient of the order of unity.

In order to find the value of this coefficient we must determine accurately the position of the Fermi level μ for $T \rightarrow 0$. This can be done if we know the energy distribution of the donor states. Miller and Abrahams [13] calculated μ and C on the assumption that the probability of enhancement of the donor energy by an amount ε is proportional to the probability that an acceptor is located at a distance $e^2/\kappa \varepsilon$ from this donor. However, they ignored the possibility that a second vacant donor might be located near the acceptor and the potential of this donor could alter strongly the energy of the first donor. Consequently, the value $C = 1.61$ found in [13] differs considerably from $C = 0.99$ obtained in [10, 11]. We shall now reproduce the general arguments given in [10, 11] and compare in detail the results derived in this way with the experimental

data. In order to find the Fermi level in a semiconductor with $K \ll 1$, we shall consider the donors located in the direct vicinity of an acceptor and we shall ignore the interaction between these donors and the other acceptors (this interaction will be allowed for later). We shall then determine the number of ionized donors in the vicinity of one acceptor, corresponding to some positive value of μ (like all the energies, the Fermi level will be measured upward from the level of an isolated impurity). We may find that there is not a single ionized donor near any given acceptor (this will be known as the 0-type complex). This can happen in the case of an accidental donor-depletion region around an acceptor: In this case the increase in the energy of an electron located at a donor which results from the presence of the nearest negative acceptor does not exceed μ . We can also have a situation in which there is only one ionized donor near an acceptor (1-type complex). Finally, we shall consider the case when there are two ionized donors near an acceptor (2-type complex). We shall postulate that these donors are located in such a way that the level energies at each of them are raised above μ because the potential generated by an acceptor at any of the donors is considerably greater than the potential due to the presence of the second donor. Such a complex may form when two donors are located close to an acceptor but are on opposite sides of the latter. Examples of 0- and 2-type complexes can be seen in Fig. 9.

We can easily show that, in the case of positive μ , we cannot have three ionized donors near one acceptor. An equilateral triangle with the ionized donors at the three corners and the acceptor at the center represents a configuration which is extremal in the sense of the maximum proximity of all three donors to the acceptor and the maximum remoteness of these donors from one another. However, a simple calculation of the energy shift of each of the donors shows that even in this case this shift is negative.

It follows that the 0-type complexes are negatively charged, whereas the 2-type complexes are positively charged. The chemical potential μ is governed by the condition of neutrality, i.e., by the condition that the concentrations of the 0- and 2-type complexes $N_0(\mu)$ and $N_2(\mu)$ are equal. The concentration $N_0(\mu)$ can be found quite easily. We know that a 0-type complex exists when there are no donors at distances $r_\mu = e^2/\kappa\mu$ from a fixed acceptor. The probability of this situation is $\exp(-4\pi N_D r_\mu^3/3)$. Thus, we find that $N_0(\mu)$ is given by

$$N_0(\mu) = N_A \exp\left(-\frac{4\pi}{3} \frac{e^6 N_D}{\kappa^3 \mu^3}\right). \quad (39)$$

Calculation of $N_2(\mu)$ is much more difficult. The results of computer calculations of $N_2(\mu)$ are reported in [10, 11]. Next, we can calculate the chemical potential μ . We thus find that

$$\epsilon_3 = \mu = 0.99 \frac{e^2 N_D^{1/3}}{\kappa}. \quad (40)$$

The precision of the computational procedure used in [10, 11] for ϵ_3 is in excess of 1%. It is interesting to note that the concentration of the 0-type complexes corresponding to the value of μ defined by Eq. (40) is 1.3% of the total acceptor concentration. This can be shown by substituting Eq. (40) into Eq. (39). The number of the 2-type complexes is the same. The other 97.4% of the acceptors form neutral 1-type complexes. The nature of the random distribution of donors around an acceptor determines which complexes are formed. The distributions of the different complexes in space are random.

We have ignored the influence of electric fields of the charged complexes on the energy levels of the remote donors, which is justified only for very small values of the degree of compensation K . This influence must be allowed for if we wish to find the correction to ϵ_3 which contains K . We have already mentioned that the concentrations of the positively charged 2-type complexes and the negatively charged 0-type complexes are equal for the crystal as a whole. However, because of the random distribution of complexes, a given finite volume may have an excess or deficiency of charges of particular sign. Such fluctuations of the charge density give rise to fluctuations of the large-scale electrostatic potential $\varphi(r)$, which modulate the energy levels of donors. It is shown in [11] that this modulation leads to a correction proportional to $K^{1/4}$ and the final expression for ϵ_3 obtained for low values of K is

$$\epsilon_3 = 0.99 \frac{e^2 N_D^{1/3}}{\kappa} (1 - 0.3K^{1/4}). \quad (41)$$

We have already mentioned that Miller and Abrahams [13] found ϵ_3 , ignoring the existence of the 0- and 2-type complexes, i.e., they used an incorrect energy distribution of the donor levels. Their result for $K \ll 1$ is

$$\epsilon_3 = 1.61 \frac{e^2 N_D^{1/3}}{\kappa} (1 - 1.35K^{1/4}). \quad (42)$$

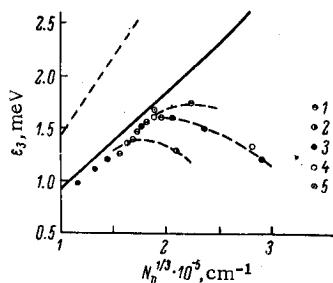


Fig. 10. Dependence of the activation energy ϵ_3 of hopping conduction in germanium on the concentration of principal impurities in weakly compensated samples: 1) phosphorus-doped germanium [12]; 2) gallium-doped germanium [41]; 3) antimony-doped germanium [17]; 4) two antimony-doped samples [12]; 5) the same two samples under "maximal" uniaxial compression. The continuous straight line is the theoretical dependence (41) plotted for $K = 0$. The dashed line represents the Miller and Abrahams equation (42) for $K = 0$.

Equation (41) differs quite strongly from Eq. (42). At the lowest values of K this difference amounts to 60%. We shall now show that the experimental results support Eq. (41).

Figure 10 shows the dependence of the experimentally determined activation energy ϵ_3 on the concentration of the principal impurities in weakly compensated samples of n- and p-type germanium [12, 17, 41]. The continuous straight line represents the results obtained in [10, 11], which are given by Eq. (41) for $K = 0$. The dashed line shows the dependence which follows from the Miller and Abrahams equation corresponding to $K = 0$ [13]. We shall start by considering the samples with the fewest impurities. The points representing these samples lie quite close to the continuous straight line but are still below it. This small discrepancy is due to the finite degree of compensation. Estimates given in [12, 17, 41] show that the degree of compensation for their samples is $K < 0.06$. At these degrees of compensation the value of ϵ_3 of Eq. (41) should decrease by 10-15%. This is the order of magnitude of the discrepancy in Fig. 10. Thus, the experimental values of ϵ_3 obtained for low donor concentrations N_D are in good agreement with Eq. (41). Because Eq. (41) depends strongly on the degree of compensation, the same results can be matched also with Eq. (42). However, it is then necessary to assume that the accidental compensation lies within a very narrow range (3-3.5%) for the samples used in [12, 17, 41]. This assumption is artificial and very unlikely to be correct.

At higher values of the donor concentration N_D the activation energy ϵ_3 deviates from Eq. (41) and

gradually decreases to zero. This can be interpreted as follows. At low values of K the levels of most of the donors are very little perturbed and their energies are very close to one another. Therefore, the overlap of the wave functions of the resonant states leads to the formation of an impurity band of width Ω which increases exponentially with rising N_D (Fig. 11). The influence of the overlap on the position of the Fermi level is initially weak. This is because the donors present in acceptor complexes do not resonate because of the difference between the potentials which is established between them by the electric field of the complexes. The difference between the energies of electrons located at two donors near an acceptor is $\Delta \sim e^2 N_D^{1/3}/\mu$. As long as $\Omega \ll \Delta$, the shift of the donor levels in such complexes is of the order of Ω^2/Δ and is considerably smaller than the width of the impurity band. Therefore, when $\Omega \ll \Delta$, i.e., when the quantum effects in the case of ϵ_3 are still small, we can ignore the shift of the Fermi level because the dominant effect is the increase in the width of the impurity band with increasing donor concentration N_D . The states near the upper edge of the impurity band are characterized by a high mobility. Since these states are separated by very small gaps from the Fermi level, they dominate the conduction processes. Thus, the activation energy can be less than μ and can decrease rapidly with increasing N_D .

This point of view is supported by a comparison of the results obtained for germanium doped with different impurities. It is shown in Secs. 2 and 3 that the effective Bohr radii of gallium, antimony, and phosphorus are related by $a_{\text{Ga}} > a_{\text{Sb}} > a_{\text{P}}$. Therefore, the influence of the overlap at a fixed impurity concentration should be strongest for gallium, weaker for antimony, and still weaker for phosphorus. It is evident from Fig. 10 that this conclusion is in agreement with the experimental results. When the impurity concentration is increased, the overlap effects increase in importance in the same sequence (Ga, Sb, P).

The validity of the quantum treatment of the deviations from the classical law (41) is supported

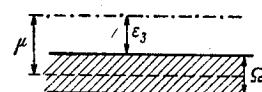


Fig. 11. Increase in the width of the impurity band as a possible cause of the reduction in ϵ_3 with increasing impurity concentration. The chain line represents the Fermi level and the dashed line is the energy of the unperturbed impurity level. The states in the impurity band are shown shaded.

even more strongly by the results obtained in studies of the influence of uniaxial pressure [12, 25]. We have already mentioned that the "volume" of a wave function and the overlap between the neighboring donor states in n-type germanium decrease under pressure. Therefore, the application of pressure should reduce strongly the deviation of ε_3 from the value given by Eq. (41). It is evident from Fig. 10 that this did indeed occur in the experiments [12] on a sample of germanium with an antimony concentration $N_D = 2.2 \cdot 10^{16} \text{ cm}^{-3}$ ($N_D^{1/3} = 2.8 \cdot 10^5 \text{ cm}^{-1}$). The value of ε_3 under pressure was found to be very close to the classical value predicted by Eq. (41). A strong rise in the activation energy was observed in [25] for the more heavily doped samples.

On the other hand, the pressure should not affect the value of ε_3 obtained for the less heavily doped samples, which satisfy approximately Eq. (41). Even in the absence of pressure, the overlap in such samples is of little importance and further reduction in the overlap cannot affect ε_3 . These comments apply to germanium with $N_D = 6.5 \cdot 10^{15} \text{ cm}^{-3}$ ($N_D^{1/3} = 1.87 \cdot 10^5 \text{ cm}^{-1}$). It is evident from Fig. 10 that, in this case, the pressure has a negligible influence on the value of ε_3 [12].

A strong magnetic field also reduces the overlap of the wave functions and, therefore, its influence on ε_3 of germanium is similar to the effect of uniaxial pressure: At low impurity concentrations a magnetic field does not affect ε_3 , but in more heavily doped samples it increases ε_3 , i.e., it balances out the deviation from Eq. (41). The latter case is illustrated clearly by the results for gallium arsenide [28] (Fig. 8), for which doubling of ε_3 is observed when the H is increased from 40 to 140 kOe. A strong increase in the activation energy due to the application of a field of 5 kOe has also been reported for n-type InSb [42]. On the other hand, the activation energy ε_3 of lightly doped epitaxial gallium arsenide films is independent of H [33].

6. ACTIVATION ENERGY ε_3 UNDER STRONG COMPENSATION CONDITIONS

If the compensation is strong ($1-K \ll 1$), the density of electrons localized at donors, $n = N_D - N_A$, is much smaller than the donor concentration N_D . Therefore, at low temperatures all the electrons can occupy donors whose energy levels are reduced considerably by the potential of the neighboring charged impurities. Consequently, the Fermi level of a strongly compensated semiconductor lies below the level of isolated impurities

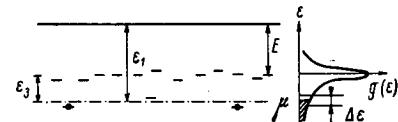


Fig. 12. Energy level scheme of a strongly compensated semiconductor (the large-scale potential is ignored). The continuous line is the bottom of the conduction band and the chain line is the Fermi level. The density of donor states is plotted on the right. The occupied states are shown shaded. The valence band and acceptor levels are not shown.

[8] (Fig. 12). The lower the electron density n , the greater is the shift of the Fermi level toward the middle of the forbidden band. The donors whose energies are close to the Fermi level are separated from one another by large distances of the order of $n^{-1/3}$ and, therefore, electron jumps between such donors are very unlikely. At moderately low temperatures, electrons are more likely to acquire energies at which the density of states is high, i.e., their energy may increase approximately to the energy of isolated impurity levels. Such electrons can then jump between donors separated by distances of the order of $N_D^{-1/3}$. Thus, to within values of the order of the average scatter of the donor levels $e^2 N_D^{1/3} / \kappa$, the activation energy ε_3 of a strongly compensated semiconductor remains equal to the separation between the Fermi level and the level of isolated impurities. Moreover, it is clear from Fig. 12 that the activation energy of the band conduction ε_1 also increases at low values of n/N_D and this increase is such that it obeys the equality

$$\varepsilon_1 = E + \varepsilon_3. \quad (43)$$

In order to find the value ε_3 as a function of N_D and n , we must determine the density of donor states $g(\varepsilon)$. If we ignore the large-scale fluctuations of the concentration of charged impurities (this effect will be considered later), we find that the donor levels with low energies appear primarily for the following reasons [8]. A given donor may be located at a distance $r \ll N_D^{-1/3}$ from another positively charged donor. If $r \gg a$, the correction ε which must be added to the energy of the level of the first donor is given simply by the Coulomb potential of the second donor, i.e.,

$$\varepsilon = -\frac{e^2}{\pi r}. \quad (44)$$

As in Sec. 5, we shall measure the values of ε and μ upward from the level of isolated impurities. When the pair of donors under consideration acquires one electron, the binding energy of a second electron to this pair is E . Therefore, when

$\mu < 0$, a pair of donors separated by a short distance has only electron. We can find $g(\epsilon)$ if we calculate the concentration of pairs which have an energy level in the interval $(\epsilon, \epsilon + d\epsilon)$. In other words, we must find the number of pairs characterized by a distance r in the range $[r(\epsilon), r(\epsilon) + (dr/d\epsilon)d\epsilon]$, where $r(\epsilon) = -e^2/\kappa\epsilon$. The probability of the occurrence of donor pairs separated by the required distance is $4\pi N_D r^2(\epsilon) (dr/d\epsilon)d\epsilon$. The concentration of pairs found in this way must be multiplied by N_D and then divided by 2 because, otherwise, each donor would be counted twice. If we use the explicit form of the function $r(\epsilon)$, we obtain

$$g(\epsilon) = \frac{2\pi N_D^2 e^8}{\epsilon^4 \kappa^3}. \quad (45)$$

It is now quite easy to find the Fermi level at $T = 0^\circ\text{K}$ from the condition that

$$\int_{-\infty}^{\mu} g(\epsilon) d\epsilon = n. \quad (46)$$

In this way, we obtain

$$\epsilon_3 = |\mu| = \left(\frac{2\pi}{3}\right)^{1/3} \frac{e^2 N_D^{1/3}}{\kappa n^{1/3}} = \left(\frac{2\pi}{3}\right)^{1/3} \frac{e^2 N_D^{1/3}}{\kappa (1-K)^{1/3}}. \quad (47)$$

Equation (47) is valid if the distances separating the components of donor pairs $r \sim r_\mu = e^2/\kappa|\mu|$ are large compared with a , but small compared with the average distance between impurities $N_D^{-1/3}$. This imposes the following restrictions on ϵ_3 :

$$\frac{e^2 N_D^{1/3}}{\kappa} < \epsilon_3 < E. \quad (48)$$

The existence of a "window" between $e^2 N_D^{1/3}/\kappa$ and E is ensured by the light-doping condition $N_D a^3 \ll 1$. When r_μ becomes comparable with a , the classical equation (44) becomes inapplicable. When quantum effects are allowed for, it becomes clear that even when $r \rightarrow 0$, two donors cannot form a level deeper than $4E$. Therefore, when $r \rightarrow 0$, the value of ϵ_3 reaches $4E$ and the Fermi level is no longer shifted downward by the donor pairs.

In the analysis given above we have ignored the large-scale fluctuations of the potential which occur in the case of random impurity distributions. Such fluctuations give rise to a slow spatial modulation of all the energy levels in Fig. 12. The influence of such large-scale fluctuations on the values of ϵ_1 and ϵ_3 has been considered in detail in [8]. It has been found that the large-scale potential leads to two new effects. First, in the energy

range defined by Eq. (48), the activation energy ϵ_3 is of the form

$$\epsilon_3 = \nu_1 \frac{e^2 N_D^{1/3}}{\kappa n^{1/3}}, \quad (49)$$

i.e., we must modify Eq. (47) by replacing $(2\pi/3)^{1/3}$ with a new numerical coefficient which is of the order of unity. We can find ν_1 by means of complex computer calculations in accordance with the program suggested in [8]. The second effect is manifested by the fact that Eq. (49), but with a different numerical coefficient ν_2 , applies at energies exceeding $4E$. It must be stressed that the large-scale potential does not alter Eq. (48).

Thus, the theory shows that the value of ϵ_3 increases as $(1-K)^{-1/3}$ when $K \rightarrow 1$. In the preceding section we have shown that, in the $K \ll 1$ range, the energy ϵ_3 decreases with increasing K . It follows that the function $\epsilon_3(K)$ should have a minimum at $K \approx 0.5$. Such a minimum can be observed directly [1] or indirectly, with the aid of the negative hopping photoconductivity [43]. Unfortunately, it is not possible to calculate the exact theoretical value of ϵ_3 corresponding to $K \approx 0.5$. All that we can say is that when $K \approx 0.5$, the value of ϵ_3 is equal to $t e^2 N_D^{1/3}/\kappa$, where t is a numerical coefficient of the order of unity.

In spite of the fact that the theory of Miller and Abrahams [13] also predicts a minimum in $\epsilon_3(K)$, the results of this theory are invalid in the $K \geq 0.5$ range as well as for $K \ll 1$. Miller and Abrahams ignored the downward shift of the levels of some donors induced by the potential of the neighboring charged donors and also failed to take into account the smoothly varying potential resulting from large-scale fluctuations in the concentration of charged impurities. We have already shown that these physical phenomena are responsible for a strong rise of $\epsilon_3(K)$ in the $K \rightarrow 1$ range.

Equation (49) and the conclusions of the theory put forward in [13] are compared in Fig. 13 with the experimental data for specially compensated p-type germanium [44], reviewed in detail in [1]. We can see that, whereas the theory of Miller and Abrahams [13] predicts a weak variation of ϵ_3 in the $K \rightarrow 1$ range, the experimental results indicate a strong rise of ϵ_3 , in agreement with Eq. (49). We have mentioned earlier that ϵ_1 should increase simultaneously with ϵ_3 . An examination of Fig. 7 in the review of Mott and Twose [1] shows that the rise of ϵ_3 , which is evident in Fig. 13, is indeed accompanied by an increase in ϵ_1 by 1-2 meV.

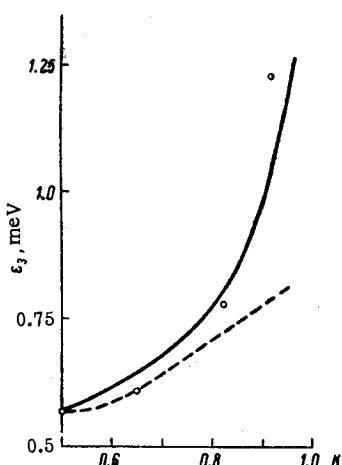


Fig. 13. Dependence of ε_3 on K . The points are the experimental results for a sample of p-type germanium with an acceptor (gallium) concentration $N_A = 2.66 \cdot 10^{15} \text{ cm}^{-3}$ [1, 44]. The continuous curve represents a graph of the function $A(1-K)^{-1/3}$, where A is selected to ensure that the curve passes through the experimentally determined point corresponding to $K = 0.5$. The dashed curve represents the theoretical dependence of Miller and Abrahams [13].

Unfortunately, the compensation of the samples studied in [44] is not sufficiently strong so that ε_3 and the rise of ε_1 are of the same order of magnitude as the average scatter of donors in respect of the energy $e^2 N_D^{1/3} / \mu$; under the experimental conditions in [44] this scatter was 1.3 meV. Therefore, a quantitative comparison of the results given in [44] with Eqs. (49) and (43) is, strictly speaking, impossible. Data on ε_1 and ε_3 were reported in [45, 46] for strongly compensated n-type germanium; these data were similar to those reported in [44]. A very strong (by 20 meV) rise of ε_1 was observed in [47, 48] for n-type Ge in the $K \rightarrow 1$ range. However, the hopping conduction was not investigated in [47, 48] so that it was not possible to check Eq. (43).

The present author is aware of only one experimental investigation in which a rise of both activation energies ε_1 and ε_3 , sufficient to make

a comparison with Eqs. (43) and (49), was observed: This was the investigation of the conduction in p-type InSb doped with Mn, Ge, and Fe [49]. Figure 14 shows four typical experimental curves. Table 1 lists the values of the corresponding impurity concentrations, degrees of compensation, and the activation energies. Samples 1 and 3 were moderately compensated. Therefore, the values of ε_3 for these samples were small and the values of ε_1 could be regarded as equal to the ionization energy of isolated Ge and Mn impurities. Samples 2 and 4 were strongly compensated and characterized by a large increase in ε_1 and ε_3 . Equation (43) is satisfied reasonably well by these two samples. The last column of Table 1 gives the values of ε_3 calculated for samples 2 and 4 with the aid of Eq. (49), in which $\nu_1 = 1$ was substituted and the corresponding values for samples 1 and 3 calculated with the aid of Eq. (41). A significant deviation from the linear dependence $\log \rho$ on T^{-1} was observed for strongly compensated samples at very low temperatures. We shall consider the origin of this deviation in the next section.

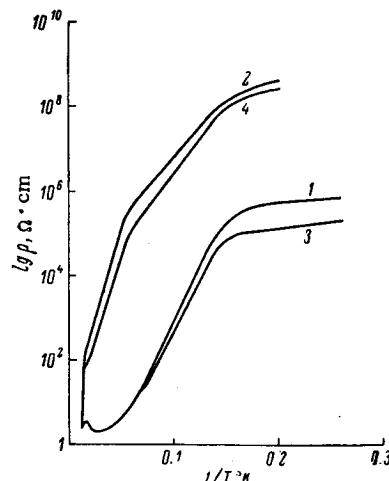


Fig. 14. Temperature dependences of the resistivity of lightly doped samples on p-type InSb. The parameters of the samples are listed in Table 1.

TABLE 1

Sample	Acceptor	$N_A - N_D, \text{ cm}^{-3}$	$N_A \cdot 10^{-14}, \text{ cm}^{-3}$	K	Activation energy		
					$\varepsilon_1, \text{ meV}$	$\varepsilon_3, \text{ meV}$	$\varepsilon_3 \text{ (theor), meV}$
1	}	Ge	$2.4 \cdot 10^{14}$	0.38	10	0.6	0.5
					17.2	6	3.5
3	}	Mn	$4 \cdot 10^{14}$	0.33	9.5	0.6	0.6
					17	7	2.2

7. HOPPING CONDUCTION WITH ACTIVATION ENERGY DECREASING AT LOW TEMPERATURES

In the preceding sections we have considered ρ_3 and ε_3 separately. We found the resistivity ρ_3 by assuming that the temperature is high and the frequency of jumps between the donors is not an exponential function of the temperature. Having calculated the paths of electrons optimal from the viewpoint of the wave-function overlap and having computed ρ_3 , we determined ε_3 . We found that in the $K \ll 1$ and $1-K < 1$ range the optimal paths pass between donors with unperturbed values of the energy. Thus, the energy ε_3 in both cases is determined simply by the gap between the Fermi level and the unperturbed level of the donor impurities. Obviously, this method of calculating the resistivity is incorrect if the temperature is low, because then the temperature affects the choice of the optimal paths and alters considerably their shape. Mott [5] has shown that at low temperatures the hopping conductivity does not have an activation energy but depends on T , in accordance with the law

$$\sigma \propto \sigma_0 \exp \left\{ -\left(\frac{T_0}{T} \right)^{1/4} \right\}. \quad (50)$$

We shall now give the derivation of Eq. (50) and find the temperature at which the transition from Eq. (1) to Eq. (50) occurs in semiconductors with different values of K . We shall start from the expression for the frequency of jumps between a pair of donors:

$$\Gamma_{ij} \propto \left| \int \psi_i \psi_j d^3r \right|^2 f(\varepsilon_i) (1 - f(\varepsilon_j)) \begin{cases} N(\varepsilon_j - \varepsilon_i), \\ -\varepsilon_j > \varepsilon_i, \\ N(\varepsilon_i - \varepsilon_j) + 1, \\ \varepsilon_i > \varepsilon_j, \end{cases} \propto \exp \left(-\frac{2r_{ij}}{a} \right) \exp \left(-\left(\frac{\varepsilon_{ij}}{T} \right)^{1/4} \right), \quad (51)$$

where $f(x)$ and $N(x)$ are the Fermi and Planck distribution functions of electrons and phonons; ε_i and ε_j are the energies of the ground states of the donors i and j . The quantity $\varepsilon_{ij} = 1/2 (|\varepsilon_i - \mu| + |\varepsilon_j - \mu| + |\varepsilon_i - \varepsilon_j|)$ results from the multiplication of the distribution functions. Equation (51) is restricted, for the sake of simplicity, to isotropic wave functions $\psi_i(r)$. At very low temperatures the temperature factor in Eq. (51) leads to electron jumps which are restricted to those donors whose energy levels lie in a narrow band on both sides of the Fermi level (Fig. 12). If the width of

this band is $\Delta \varepsilon$, the concentration of the " $\Delta \varepsilon$ donors" is $\Delta N = \Delta \varepsilon g(\mu)$, where $g(\mu)$ is the density of states at the Fermi level. We shall now find the conductivity for the subset of donors with a fixed value of $\Delta \varepsilon$. For this purpose we shall replace ε_{ij} in Eq. (51) with its maximum value $\Delta \varepsilon$ (this replacement does not alter the order of magnitude of the argument of the exponential function for most of the jumps involved). We shall assume that the $\Delta \varepsilon$ donors are distributed randomly in space. Then the problem of finding the conductivity associated with the $\Delta \varepsilon$ subset reduces to the problem of the percolation in a system with an impurity concentration ΔN , which has been solved above. Therefore, the conductivity associated with the $\Delta \varepsilon$ subset can be written in the form

$$\sigma(\Delta \varepsilon) = \exp \left(-\frac{a}{(\Delta N)^{1/3} a} \right) \exp \left(-\frac{\Delta \varepsilon}{T} \right). \quad (52)$$

When $\Delta \varepsilon$ increases because of an increase in the average distance between the $\Delta \varepsilon$ donors, the first factor in Eq. (52) decreases rapidly. However, the second factor rises rapidly when $\Delta \varepsilon \rightarrow 0$. Therefore, $\sigma(\Delta \varepsilon)$ has a sharp peak at some value $\Delta \varepsilon = \Delta \varepsilon_0$. The conductivity of the whole crystal is determined by the optimal subset of donors. The expression for $\Delta \varepsilon_0$ is

$$\Delta \varepsilon_0 = \frac{T^{3/4}}{(g(\mu) a^3)^{1/4}}. \quad (53)$$

In the above expression for $\Delta \varepsilon_0$ we have omitted the numerical factor because the replacement of ε_{ij} with $\Delta \varepsilon$ does not allow us to find the coefficient in the argument of the exponential function. Substituting Eq. (53) in Eq. (52), we obtain Eq. (50) and the value of T_0 is then given by

$$T_0 = \delta (g(\mu) a^3)^{-1}. \quad (54)$$

The coefficient δ cannot be found in this way and a more complex theory developed in [50] is needed for its calculation. According to [50], $\delta \approx 16$ (see also [51]).

The temperature T_C at which the transition from Eq. (1) to Eq. (50) takes place is given by the equation

$$\exp \left(-\frac{a}{N_0^{1/3} a} \right) \exp \left(-\frac{\varepsilon_3}{T_C} \right) \simeq \exp \left\{ -\left(\frac{T_0}{T} \right)^{1/4} \right\}. \quad (55)$$

The values of T_0 and T_C for specific semiconductors can be found by discussing separately the cases of weak ($K \ll 1$), intermediate ($K \approx 0.5$), and strong ($1-K \ll 1$) compensation.

I. $K \ll 1$. If $K \ll 1$, the Fermi level lies above the level of isolated impurities and the gap between them is given by Eq. (40). The density of states above the Fermi level is N_A . Therefore, an order-of-magnitude estimate of $g(\mu)$ gives $N_A \times (e^2 N_D^{1/3} / \mu) = g_0 K$, where $g_0 = N_D^{2/3} \mu / e^2$. Substituting $g(\mu)$ in Eqs. (54) and (55), we obtain

$$T_0 \simeq \delta (g_0 K a^3)^{-1}, \quad T_C \simeq \frac{e^2 N_D^{2/3} a}{\mu} K^{1/3}. \quad (56)$$

II. $K \simeq 0.5$. In this case, the Fermi level lies in the region of the maximum of $g(\varepsilon)$. Therefore, we find that $g(\mu) = N_D (e^{-2} N_D^{1/3} / \mu)^{-1} = g_0$, and the expressions for T_0 and T_C become

$$T_0 \simeq \delta (g_0 a^3)^{-1}, \quad T_C \simeq \frac{e^2 N_D^{2/3} a}{\mu}. \quad (57)$$

III. $1-K \ll 1$. The density of states $g(\mu)$ for $K \rightarrow 1$ can be obtained by substituting Eq. (47) in Eq. (45). In this way we obtain $g(\mu) = g_0 (1-K)^{1/3}$ and

$$T_0 \simeq \delta (g_0 a^3)^{-1} (1-K)^{-4/3}, \quad T_C \simeq \frac{e^2 N_D^{2/3} a}{\mu}. \quad (58)$$

Our quantitative results, represented by Eqs. (56)–(58), are in agreement with the qualitative conclusions of Pollak [52] pertaining to the transition from Eq. (1) to Eq. (50).

It is evident from Eqs. (56)–(58) that the temperature T_C is very small in the $K \ll 1$ range. For $K \simeq 0.5$ and in the $1-K \ll 1$ range, the temperatures T_C are of the same order of magnitude and proportional to $N_D^{2/3}$. It follows that the law (50) should be obeyed at moderately low temperatures by a semiconductor with $K \gtrsim 0.5$ and a moderately low donor concentration N_D . Doping must not be too weak also because the resistivity in the $T \ll T_C$ range should remain within the limits of the experimental error. On the other hand, the doping must be too strong or the conduction will be metallic. If a semiconductor is strongly compensated, the transition to the metallic conduction occurs at higher values of N_D [1, 6]. Therefore, in order to observe the conditions corresponding to Eq. (50) one should use a strongly compensated sample with $N_D a^3 \ll 1$. The conductivity of strongly compensated samples of n-type InSb [42], CdTe [53], and Ge [54] with approximately correct values of $N_D a^3$ do indeed exhibit a gradual fall in the activation energy and their conductivity varies approximately in accordance with Eq. (50). This gradual fall in the activation energy is also observed in

germanium with $K = 0.4$ and with impurity concentrations quite close to the critical concentration necessary for the transition to the metallic state [55]. The fall in the activation energy observed in weakly doped samples of p-type InSb at very low temperatures (Fig. 14) is also probably due to the approach to the conditions described by Eq. (50). Thus, experimental data on crystalline semiconductors support the law (50). In earlier papers it has been demonstrated that the conductivity of amorphous films of Ge, Si, and C is described satisfactorily by Eq. (50) (see, for example, [50]).

We shall now discuss in greater detail the theoretical assumptions on which the derivation of Eq. (50) is based. In writing Eq. (52), we have assumed that the distribution of the $\Delta\varepsilon$ donors in space is random. It is quite clear that the energies of donors in the $K \ll 0.5$ case are correlated only over distances of the order of $N_D^{-1/3}$. The donors of the $\Delta\varepsilon$ subset are separated from one another by large distances and, therefore, their positions in space are absolutely random. If we ignore the large-scale potential, we find that the same situation applies also to $K \rightarrow 1$. This large-scale potential modulates spatially the density of donor states located at the Fermi level. If $\varepsilon_1 < 4E$, this modulation is slight [8]. However, if $\varepsilon_1 > 4E$, the modulation is very strong and an electron must tunnel across potential humps. In this case, the decrease in the activation energy with decreasing temperature should not be given by Eq. (50). However, at sufficiently low temperatures, when the length of a jump $[g(\mu) \Delta\varepsilon]^{-1/3}$ exceeds the correlation radius of the large-scale potential, the distribution of the $\Delta\varepsilon$ donors should again become random and Eq. (50) should apply.

The most important assumption made in the derivation of Eq. (50) is the same as that employed in all other cases in the theory of hopping conduction, i.e., that the wave functions are strongly localized and the energies of donors exhibit a large scatter [56]. Although a rigorous proof of this assertion cannot be provided, there are good reasons for believing it to be correct. All the experimental data reviewed in the present paper support this assertion. The decisive experimental evidence in support of the localization of the wave functions would be the absence of the temperature-independent conductivity at $T \rightarrow 0$ and verification of Eq. (50). However, since the dependence $\log \sigma \propto T^{-1/4}$ is weak, a very wide temperature range would be needed in order to check Eq. (50). Therefore, it seems that a more convenient method for verifying the Mott model would be a study of the mag-

netoresistance under the conditions corresponding to Eq. (50).

The theory of the magnetoresistance in moderate magnetic fields, which do not alter the percolation paths, can be developed in a manner similar to the derivation of Eq. (26) in Sec. 4. The only difference is that in the region where the law (50) is obeyed, the lengths of electron jumps are not equal to $N_D^{-1/3}$, but to the average distance $\bar{R}(T)$ between the $\Delta\varepsilon$ donors. It follows from Eq. (53) that

$$\bar{R}(T) = (g(\mu)\Delta\varepsilon)^{-1/3} = a \left(\frac{T_0}{T} \right)^{1/4}.$$

If we substitute $\bar{R}(T)$ into the expression for the probability of a jump (23), we obtain

$$\frac{p(H)}{p(0)} = \exp \left\{ s_1 \frac{a^3 H^2}{mc^2} \left(\frac{T_0}{T} \right)^{1/4} \right\}, \quad (59)$$

where s_1 is a coefficient of the order of 0.1 (a more detailed theory of the type given in [50] is needed to find the exact value of this coefficient).

It is evident from Eq. (59) that the dependences of the magnetoresistance on H and T are quite strong and, therefore, these dependences could be verified experimentally quite easily.

In very strong magnetic fields, for which the argument of the exponential function in Eq. (59) is larger than the argument in Eq. (50), it is necessary to make an allowance for changes in the percolation paths in the magnetic field. In this case, the conductivity associated with the $\Delta\varepsilon$ donor subset is proportional to $\exp(-L_C) \exp(-\Delta\varepsilon/T)$ and the relationship of L_C with ΔN and $\Delta\varepsilon$ can be found from the condition $\pi\lambda^2 L_C^2 a \Delta N = \beta_p$, which is obtained from Eq. (32) by the replacement of N_D with ΔN . If we express L_C in terms of $\Delta\varepsilon$ and find the optimal $\Delta\varepsilon$ subset and the associated conductivity, we finally obtain

$$\frac{p(H)}{p(0)} = \exp \left\{ s_2 \left[\frac{eH}{\hbar c g(\mu) a_H T} \right]^{1/4} \right\}. \quad (60)$$

The transition from Eq. (59) to Eq. (60) occurs when $R(T)$ becomes of the order of λ^2/a , i.e., it occurs in a field $H \simeq \hbar c g(\mu) T^{1/4}/a^{5/4}$.

The author is grateful to A. L. Efros for reading the manuscript and for his valuable advice, and to O. V. Emel'yanenko, D. N. Nasledov, D. D. Nedoglo, I. N. Timchenko, E. M. Gershenson, V. S. Ivleva, V. A. Il'in, I. N. Kurilenko, L. B. Litvak-Gorskaya, M. Pollak, N. V. Agrinskaya, and E. D. Krylovaya for making their papers [33, 42, 49, 52, 53] available before publication.

APPENDIX

We shall consider in detail the derivation of Eqs. (23) and (27) and the relationship between them. We shall assume that a donor is located at the origin of a cylindrical system of coordinates (ρ, φ, z) with its z axis directed along the magnetic field. We shall assume that the vector potential \mathbf{A} is in the form $A_\varphi = 1/2 H \rho$, $A_z = A_\rho = 0$. Then, the Schrödinger equation for the ground state of an electron attached to a donor is of the form [57]

$$-\frac{\hbar^2}{2m^*} \Delta \psi + \frac{e^2 H^2 \rho^2}{8m^* c^2} \psi - \frac{e^2}{z \sqrt{\rho^2 + z^2}} = -E_H \psi. \quad (61)$$

Here, E_H is the energy of the ground state ($E_H > 0$). In deriving Eq. (61) we have taken into account the fact that the wave function of the ground state has cylindrical symmetry and is independent of the angle φ . We shall find the asymptotic behavior of $\psi(\rho, z)$ in the plane $z = 0$ and assume that ρ is large. In the region in which the wave function is exponentially small it can be found by the quasi-classical method. We shall write $\psi(\rho, z)$ in the form

$$\psi(\rho, z) = B(\rho, z) e^{\frac{iS(\rho, z)}{\hbar}}. \quad (62)$$

Substituting Eq. (62) into Eq. (61), we obtain the Hamilton-Jacobi equation for $S(\rho, z)$:

$$\left(\frac{\partial S}{\partial z} \right)^2 + \left(\frac{\partial S}{\partial \rho} \right)^2 = 2m^* \left(-E_H + \frac{e^2}{z\rho} - \frac{e^2 H^2 \rho^2}{8m^* c^2} \right). \quad (63)$$

The ground-state wave function should be symmetric with respect to the $z = 0$ plane and, therefore, $(\partial S/\partial z)_{z=0} = 0$. Integration of Eq. (63) then gives

$$S(\rho, z=0) = \int_0^\rho \sqrt{2m^* \left(-E_H + \frac{e^2}{z\rho} - \frac{e^2 H^2 \rho'^2}{8m^* c^2} \right)} d\rho'. \quad (64)$$

The constant of integration in Eq. (64) is selected in such a way that the wave function is not exponentially small for $\rho = z = 0$.

Since $E_H \geq \hbar^2/m a^2$, the Coulomb potential at distances $\rho \gg a$ is small compared with E_H . At large distances this potential affects only the pre-exponential function in Eq. (62). We are interested in the argument of the exponential term in the wave function and, therefore, we can ignore the term $e^2/\kappa\rho$ in Eq. (64). Then, having written E_H in the form $E_H = \hbar^2/2m^* a^2$, we obtain

$$S(\rho) = i\hbar \int_0^\rho \sqrt{\frac{\rho'^2}{a_H^{-2} + \frac{\rho'^2}{4\lambda^4}}} d\rho'. \quad (65)$$

We shall first consider the case $\lambda \gg a$, when the magnetic field does not alter the energy of the ground state of a hydrogen-like atom and $a_H = a$. In this case, Eq. (65) leads to different results at moderate ($a \ll \rho \ll \lambda^2/a$) and very large ($\rho \gg \lambda^2/a$) distances from the impurity atom. If $\rho \ll \lambda^2/a$, we can expand the integrand in Eq. (65) in terms of $\rho^2 a^2/4\lambda^4$ and, retaining the first two terms of the expansion, we find that

$$S(\rho) = i\hbar \left(\frac{\rho}{a} + \frac{\rho^3 a}{24\lambda^4} \right) \quad (a \ll \rho \ll \frac{\lambda^2}{a}). \quad (66)$$

Substituting Eq. (66) into Eq. (62), we obtain

$$\psi(\rho) \propto \exp\left(-\frac{\rho}{a}\right) \exp\left(-\frac{\rho^3 a}{24\lambda^4}\right) \quad (a \ll \rho \ll \frac{\lambda^2}{a}). \quad (67)$$

At large distances $\rho \gg \lambda^2/a$ we can ignore the term a_H^{-2} in Eq. (65) and we then obtain

$$\psi(\rho) \propto \exp\left(-\frac{\rho^2}{4\lambda^2}\right) \quad (\rho \gg \frac{\lambda^2}{a} \gg a). \quad (68)$$

In the limit of very strong magnetic fields, represented by $\lambda \ll a$, Eq. (65) shows that the wave function is described by Eq. (68) at all distances at which it is exponentially small.

In the range of fields considered by Mikoshiba [$\lambda > a/(N_D a^3)^{1/6}$, $N_D a^3 \ll 1$] [34], the average distance between the impurities $N_D^{-1/3}$ satisfies the condition $\rho \ll \lambda^2/a$ and the overlap integral can be calculated if we use the transverse asymptotic expression (67). This leads to Eq. (23).

If $\lambda < a/(N a^3)^{1/6}$ (irrespective of the relationship between λ and a), the inequality $\rho > \lambda^2/a$ is satisfied at distances $\rho = N_D^{-1/3}$ and the wave function is given by Eq. (68). In this case, the overlap integral is calculated by means of Eq. (27) and this leads to the jump probability given by Eq. (28). In calculating the overlap integrals in Eqs. (23) and (28), we have made allowance for the fact that when the origin of the coordinate system for A coincides with the impurity i, the function ψ_j acquires an additional (compared with ψ_i) phase factor $\exp\{-ie[H_{ij}r/2\hbar c]\}$ [58].

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