

# Percolation theory and conductivity of strongly inhomogeneous media

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Percolation theory is the name given a new mathematical discipline, initiated in 1957 and found to be unusually productive in the physics of inhomogeneous systems. The main purpose of the review is to describe the recently rapidly developing theory of the electric conductivity of strongly inhomogeneous media, which leads to questions of percolation theory. This gives rise to new problems in percolation theory, namely continual problems and problems dealing with random sites. The methods of solving these problems and the main results are described in detail. Particular attention is paid to the behavior of various quantities near the percolation threshold, and the theory of critical exponents and the similarity hypothesis in percolation theory are treated in detail for the first time. The main objects to which the theory is applied are amorphous and weakly-doped crystalline semiconductors. The main results of the theory of hopping conductivity of such semiconductors are reported, namely, the exponential temperature and concentration dependences, the theory of magnetoresistance, and the theory of the conductivity of films. The structure of the pre-exponential terms is also discussed.

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## 1. INTRODUCTION

In 1957, Broadbent and Hammersley<sup>[1]</sup> formulated new mathematical problems connected with processes which the authors called percolation processes. On the basis of these problems, a mathematical discipline was created, called percolation theory, and found extensive use in various branches of physics of the condensed state. We start with naming a few typical problems of percolation theory and with an explanation of the processes that are described by these problems.

The classical problems of percolation theory are lattice bond and site problems. We consider a three-dimensional lattice and assume that a certain liquid can flow from one site to another along tubes, which we shall call bonds. We shall say that, with the aid of these bonds, each wetted site wets its nearest neighbors. It is obvious that one wetted atom must cause the wetting of the entire lattice. By introducing into this system stochastic elements in various ways, we obtain the bond and site problems. We discuss first the bond problem. We assume that each bond in the lattice can be broken with a probability  $1-x$  that does not depend on the state of the other bonds. We assume that one lattice site with partially broken bonds is wetted and we discuss the question of how many other sites of the lattice it can wet. As already mentioned, at  $x = 1$  the entire lattice is wetted with a probability equal to unity. It is clear that in the case of small  $x$  only a finite number of sites is wetted, since the broken bonds do not permit the liquid to move far from the initial site. One of the aspects of the bond problem is to find the value  $x_c(b)$ , the minimum value of  $x$  at which the probability that the initial site wets an infinite number of other sites differs from zero. We shall call the point  $x_c(b)$  the percolation threshold. The bond problem describes, for

example, the process of percolation of current through a lattice in which instead of unbroken bonds there are equal resistances that join the neighboring sites, and the broken bonds correspond to infinite resistance. The effective electric conductivity  $\sigma$  of such a medium differs from zero only if  $x > x_c(b)$ . The determination of the value of  $\sigma(x)$  is a different aspect of the bond problem.

We now discuss the site problem. In this problem, all the bonds are assumed unbroken, but the sites are spoiled. Sites can be closed or open, closed sites do not let the liquid flow in any direction. They cannot be wetted and do not wet other sites. It is possible to introduce a critical fraction of open sites  $x_c(s)$ , at which the probability that a given site will wet an infinite number of other sites vanishes. The most important example of the site problem is that of a dilute ferromagnet. Imagine a solid solution of ferromagnetic material in nonmagnetic material, the fraction of the ferromagnetic atoms being equal to  $x$ . We assume that the exchange in direction between the ferromagnetic atoms, which leads to parallel orientation of their magnetic moments, decreases so strongly with distance that it can be regarded as different from zero only when these atoms are in neighboring lattice sites. We shall call sites in which the nonmagnetic atoms are situated closed. At zero temperature, all the open sites that wet each other have the same orientation of the magnetic moments. At small values of  $x$ , isolated groups (clusters) of sites that wet each other are produced. Inside each group the moments are identically oriented, but the mutual orientation of the moments of these groups is arbitrary, so that the macroscopic moment is equal to zero. The quantity  $x_c(s)$  determined from the solution of the site problem formulated above is indeed the fraction of ferromagnetic atoms in which an

infinite cluster (IC) of atoms that wet each other is first produced, i.e., a macroscopic magnetic moment arises at sufficiently low temperature. Thus, a ferromagnetic transition is possible in the considered system only at  $x > x_c(s)$ . In addition to finding the percolation threshold  $x_c$ , percolation theory deals with the fraction of sites belonging to IC at  $x > x_c$ . For a solid solution, this quantity has the meaning of the saturation magnetization. Increasing attention is being paid of late to the topology of IC. In the simplest problems formulated above, the topology of the IC determines the value of  $\sigma(x)$  and the transition temperature  $T_C(x)$ .

It should be clear from the foregoing examples that an important role in percolation-theory problems is played by random properties of the medium that are fixed in space, and by the connectivity of region with identical properties.

Applications of percolation theory are quite valid and unexpected. For example, in<sup>[1]</sup> is given the following problem: An orchard is planned in the form of a square lattice with trees in its sites. It is known that a sick tree infects another tree located at a distance  $r$  away from it with a probability  $f(r)$ , where  $f(r)$  is a rapidly decreasing function. It is required to find the minimum distance between trees, at which one sick tree is capable of infecting only a finite number of trees. Obviously, this problem reduces to the bond problem described above, and the sought distance is determined by the condition  $f(r) = x_c(b)$ , where  $x_c(b)$  is the critical value of the fraction of the unbroken bonds.

At the present time, the most important field where percolation theory is used is undoubtedly the theory of disordered systems. The main concepts of the electron theory of amorphous semiconductors, such as the mobility threshold or the percolation level, owe their existence to this new mathematical discipline. As early as in 1958, one year after the publication of the trailblazing paper<sup>[1]</sup>, Anderson<sup>[2]</sup> used the ideas of percolation theory to prove the fundamental statement concerning localization of electrons in a random potential field in the case of a sufficiently large degree of disorder. This phenomenon is called the Anderson transition, and its study is the subject of a large number of papers (see, e.g.,<sup>[3]</sup>). The ideas of percolation theory were used to calculate the mobility of electrons in helium vapor<sup>[4]</sup>, to describe metal-dielectric transitions in strongly doped semiconductors<sup>[5]</sup>, in tungsten bronzes<sup>[6,7]</sup>, in liquid mercury with decreasing density,<sup>[8]</sup> and in many other objects. As already mentioned, percolation theory was used to calculate the saturation magnetization and the Curie temperature of ferromagnetic solid solutions as functions of the concentration of the ferromagnetic atoms<sup>[9]</sup> and to study other magnetic properties of these systems.<sup>[10]</sup>

In 1971, the authors of the present review<sup>[11]</sup> and Ambegaokar, Halperin, and Langer<sup>[12]</sup> have shown that the transport of current in a disordered system with localized states, which is realized by hopping of electrons from one state to another, should be regarded as a percolation process. Both papers contained a criticism of the results of Miller and Abrahams<sup>[13]</sup>, which at that time were universally accepted, and also the idea which permitted the problem of calculating the exponent of the electric conductivity to be reduced to the problem of percolation theory. (A year later the same ideas were independently advanced by Pollak<sup>[14]</sup>.)

During the last three years, much progress was made in the theory of hopping conductivity, both in the explanation of extensive experimental data, and in the clarification of its logical construction. The mathematical formalism of the theory is completely based on the ideas of percolation theory. In addition to the previously well known lattice problems of percolation, it was necessary to use here also continual problems and random-site problems.

The exposition of percolation theory is the subject of the good reviews of Shante and Kirkpatrick<sup>[15]</sup>, of Domb, Frisch and Hammersley, and Essam<sup>[16]</sup>. The purpose of the present review is not merely to report the latest results in this field. We wish to show how the methods of percolation theory make it possible to construct a physical theory of transport phenomena in strongly inhomogeneous media. By way of application we use mainly hopping conductivity of weakly doped semiconductors. However, we do not attempt to describe the results in detail and to compare them with the experimental data, since this would call for a detailed exposition of the theory of impurity electronic states, generalized to include the case of a nonstandard spectrum, and would lead us away from the main problem. (These results are treated in sufficient detail in a review by one of us<sup>[17]</sup>.) In view of the novelty of the methods, we undertake in this review to describe most clearly the main ideas, since we hope that they turn out to be useful also in other physical problems.

In the second chapter of the review we discuss threshold points and the methods of their determination. In the third chapter we establish the connection between the exponent of the electric conductivity of an inhomogeneous medium and the threshold values of the percolation-theory problems. In the fourth chapter, on the basis of this connection, we construct the theory of the exponential dependences of the hopping conductivity on the impurity concentration, on the temperature, and on the magnetic field. Finally, the fifth chapter is devoted to an explanation of the character of the singularities of the various quantities at the threshold point. This makes it possible to find the pre-exponential factor of the hopping conductivity and to investigate size effects.

## 2. LATTICE AND CONTINUAL PROBLEMS OF PERCOLATION THEORY

Lattice problems are historically the first and the most thoroughly investigated problems of percolation theory. Many important physical problems can be reduced to them (for example, the theory of ferromagnetic solid solutions), and with them as examples it is possible to become acquainted with the methods of percolation theory; in addition, results obtained with their aid are frequently universal.

In the analysis of lattice problems one introduces the quantity  $P_N(x)$ , which is the probability that a given site wets at least  $N - 1$  other sites, i.e., belongs to a cluster of at least  $N$  sites that are bound to one another. One of the problems of the theory is to find the function

$$P(x) = \lim_{N \rightarrow \infty} P_N(x), \quad (2.1)$$

which is the probability that a given site wets an infinite number of sites. In other words,  $P(x)$  is the fraction of the lattice sites belonging to the IC. Of course, the function  $P(x)$  is not the same for the site problem as for the bond problem, and we shall designate them by the

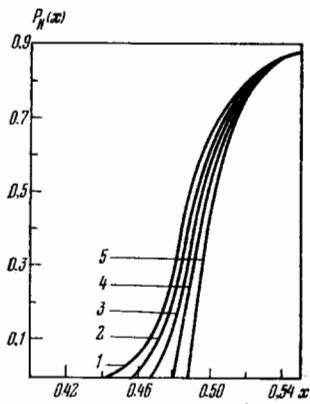


FIG. 1. The function  $P_N(x)$  for the bond problem on a two-dimensional square lattice. From the data of [19] for  $N = 667$  (1), 1000 (2), 2000 (3), 6000 (4), and  $\infty$  (5).

superscripts "s" and "b", respectively. As shown by Hammersley<sup>[18]</sup>,

$$P_N^s(x) \leq P_N^b(x). \quad (2.2)$$

From (2.1) and (2.2) it follows also that

$$P^s(x) \leq P^b(x). \quad (2.3)$$

Figure 1 shows the functions  $P_N(x)$  obtained for the bond problem with the aid of a computer in<sup>[19]</sup>. It is seen that at finite values of  $N$  these functions never vanish; the probability of finding a large but finite cluster of bound sites is always finite. We see also that as  $N \rightarrow \infty$  the function  $P_N(x)$  tends to zero at  $x \rightarrow x_c(s)$ . The function  $P(x) = 0$  at  $x < x_c$  and increases monotonically at  $x > x_c$ . This situation is analogous to a second-order phase transition, which, like all phase transitions, takes place only in an infinite system. The role of the order parameters is played in this case by the concentration of the sites belonging to the infinite cluster<sup>[20]</sup>. (We shall discuss the analogy with phase transitions in detail in Chap. 5.)

Several methods are used to determine  $x_c$ . In a large number of papers<sup>[19,21,22]</sup>  $x_c$  is determined with a computer by the Monte Carlo method. The  $P_N(x)$  are extrapolated in this case to  $N = \infty$ . In addition, the series method of Domb and Sykes is used.<sup>[23]</sup> The average of sites that wet one another is represented by a series in powers of  $x$ . It is easy to show that this series converges at small  $x$ . This proves that at small  $x$  we have  $P(x) = 0$ . The quantity  $x_c$  is the radius of the convergence of this series. Sykes and Essam<sup>[24]</sup> have proposed a rather exact method of calculating  $x_c$ , based on the analysis of the coefficients of this series for different lattices. The results  $x_c(b)$  and  $x_c(s)$  for the bond and site problems are listed in the table, which is taken from the review<sup>[15]</sup>. They differ little from the results obtained by the Monte Carlo method. For some planar lattices, the same authors<sup>[25]</sup> succeeded in obtaining exact results. These results are underlined in the table.

An analysis of the values of  $x_c$  allows us to draw a number of interesting conclusions. From the fact that  $P(x)$  is monotonic and from inequality (2.3) it follows that

$$x_c(s) \geq x_c(b), \quad (2.4)$$

as is confirmed by the data in the table. We note furthermore that the values of  $x_c$  differ quite strongly from one another even for lattice with equal numbers of dimensions. This circumstance is connected prin-

Lattice	$z$	$x_c(b)$	$zx_c(b)$	$f$	$x_c(s)$	$f/x_c(s)$
Two-dimensional:						
Hexagonal	3	<u>0.6527</u>	1.96	0.61	0.700	0.427
Quadratic	4	<u>0.500</u>	2.00	0.79	0.590	0.466
Triangular	6	<u>0.3473</u>	2.08	0.91	<u>0.500</u>	<u>0.455</u>
Three-dimensional:						
Diamond	4	0.388	1.55	0.34	0.425	0.145
Primitive cubic	6	0.247	1.48	0.52	0.307	0.160
Body-centered cubic	8	0.178	1.42	0.68	0.243	0.165
Face-centered cubic	12	0.119	1.43	0.74	0.195	0.144

cipally with the number of nearest neighbors  $z$ . For the bond problem it is convenient to introduce the average number of bonds per site. If all the bonds are unbroken, then this number is equal to  $z$ ; in the presence of broken bonds it is equal to  $zx$ . It turns out that for the bond problem the critical value of  $x_c(b)$  can be obtained approximately from the condition that the average number of bonds per site be equal to a definite number that does not depend on the concrete lattice, but depends only on the number of dimensions. For two-dimensional lattices  $zx_c(b) = 2$ ,<sup>[23]</sup> and for the three-dimensional case we have  $zx_c(b) = 1.5$ .<sup>[26]</sup> The accuracy with which this rule is satisfied can be seen from the table.

An analogous quantity can be introduced also for the site problem.<sup>[27]</sup> We draw around each lattice site a sphere with radius equal to half the distance to the nearest neighbor, and let  $f$  be the ratio of the volume occupied by these spheres to the total volume. If these spheres are assigned only to open sites, then the fraction of the volume occupied by these spheres will be equal to  $xf$ . As seen from the table, the critical value  $x_c(s)$  is determined with good accuracy from the condition that this fraction of the volume be equal to  $0.45 \pm 0.02$  for two-dimensional lattices and  $0.15 \pm 0.01$  for three-dimensional lattices.

We now consider the so-called continual problems of percolation theory. We specify in an all of space a random continuous function  $V(r)$  defined by correlation relations. Without loss of generality we assume that  $\langle V(r) \rangle = 0$  (the angle brackets denote averaging). We specify a real number  $V$  and imagine that the regions of space where  $V(r) < V$  are colored black and the remaining regions white. As  $V$  varies from  $-\infty$  to  $\infty$ , the volume of the black regions changes from zero to the volume of the entire space. It is required to find the minimum value  $V = V_c$  at which there is a possibility, by starting from a certain black point, to go an infinite distance away from it by moving only through black regions. Such a problem arises, for example, if it is necessary to find the minimum energy that an electron must have to go off to a macroscopic distance in a potential  $V(\mathbf{r})$  without leaving the classically allowed regions<sup>[4,11,26,28]</sup>. The quantity  $V_c$  is called in this case the percolation energy (the percolation level).

It is easily understood that the continual problem is close to the previously formulated lattice problems. We imagine a lattice with so small a period that the function  $V(\mathbf{r})$  remains practically unchanged in the period. We fix  $V$  and assume that the bonds between the neighboring lattice sites located in the black regions are not broken, and the remaining bonds are broken. With increasing  $V$ , the fraction  $x$  of unbroken bonds increases, and the critical value  $V_c$  corresponds to the value of  $x_c$  which represents a solution of the bond

problem, which differs from that formulated earlier in that the distribution of the broken bonds over the different sites is correlated in accordance with the form of the function  $V(r)$ .

In the continual problem it is convenient to speak of the critical fraction of space which is colored black, corresponding to the onset of percolation over the black regions

$$v_c = \int_{-\infty}^{V_c} F(V) dV, \quad (2.5)$$

where  $F(V)$  is the distribution function of the quantity  $V$ . The fraction of space  $v_c$  is less sensitive to the form of the random function  $V(r)$  than the percolation level  $V_c$ .

If the statistical properties  $V(r)$  at positive and negative values are perfectly symmetrical (in particular, if  $F(V) = F(-V)$ ), then in the two-dimensional case we have  $v_c = 0.5$ <sup>[29,30]</sup>, i.e.,  $V_c = 0$ . This is easily understood by proving that in the two-dimensional case there can be no simultaneous percolation over the white region and black regions and it is impossible to have no percolation over both the white region and the black region.

In the three-dimensional case the situation is much more complicated. There exists a number of patterns in accordance with which percolation exists both over the white regions and the black regions. (It is easily understood that in the three-dimensional space the channels of the percolation over both the white and black regions takes place need not necessarily intersect.) Therefore there exist two percolation levels, upper and lower. As  $V$  increases, at  $V = V_c$ , we have first percolation over the black, and at  $V = V'_c$  the percolation over the white is stopped. If the statistical properties of  $V(r)$  are symmetrical about zero, then  $V'_c = -V_c$ , with  $V_c < 0$ . Naturally, in the three-dimensional case  $v_c < 0.5$ . We note that these considerations lead to significant conclusions concerning the optical and electrical gaps in an amorphous semiconductor.<sup>[31]</sup>

Zallen and Scher<sup>[27,28]</sup> have proposed to use for an approximate estimate of  $v_c$  the invariant  $fx_c(s)$  of the lattice site problem. This invariant has the meaning of the fraction of the volume filled with spheres centered in the open sites of the lattice, in which percolation takes place over the touching spheres. According to<sup>[27,28]</sup>,  $v_c = fx_c(s)$ . In the two-dimensional case this yields 0.45, which is close to the exact value of  $v_c$  for a symmetrical potential, and in the three-dimensional case we obtain  $v_c = 0.15$ .

A method for solving continual problems by the Monte Carlo method with a computer was developed in<sup>[32,33]</sup>. They considered mainly Gaussian potentials, for which  $\langle V(r)V(r') \rangle = K(r - r')$ , the even correlators are equal to zero, and the odd correlators break up into products of pair correlators. It was shown that for such potentials, in the three-dimensional case,  $v_c = 0.17 \pm 0.01$  and within the limits of the calculation accuracy it does not depend on the form of the kernel  $K(r - r')$ . This is possibly an exact property of Gaussian potentials, but the authors were unable to prove it. We note that for non-Gaussian potential, values of  $v_c$  that vary in a considerable range, were obtained in<sup>[33]</sup>.

We have discussed the question of the percolation threshold in two classes of problems. The same prob-

lem for a third class of problems, that of random sites, will be discussed in Chap. 4. As we shall show in the next chapter, the problem of calculating the conductivity exponent reduces to finding the percolation threshold. To prove this statement we need some information concerning the structure of the IC. It is customarily assumed<sup>[15]</sup>, although this has not been rigorously proved, that there can not exist several IC which are not bound to one another. The topological properties of the IC are the same for all classes of problems at a given number of dimensions of space. The IC can be represented in the form of a random net that fills all of space. As the threshold is approached, this net becomes increasingly loose, but at any finite value  $x - x_c > 0$  the fraction of sites belonging to this net remains finite. To calculate the pre-exponential factor of the conductivity and for a number of other problems it is necessary to have more detailed information on the topology of the IC. This information is contained in Chap. 5.

### 3. CALCULATION OF THE ARGUMENT OF THE CONDUCTIVITY EXPONENT OF STRONGLY INHOMOGENEOUS MEDIA

In this chapter we shall show that a percolation problem arises when it comes to determining the effective electric conductivity of a disordered system. For simplicity we consider first the case of a medium that can be characterized by a local specific electric conductivity  $\sigma(r)$  with a specified distribution law. If the inhomogeneity of  $\sigma(r)$  is relatively small, i.e.,  $|\sigma(r) - \langle \sigma \rangle| / \langle \sigma \rangle \ll 1$ , then the effective electric conductivity is obtained by perturbation theory.<sup>[34]</sup> In the intermediate case  $|\sigma(r) - \langle \sigma \rangle| / \langle \sigma \rangle \approx 1$ , as shown by numerical calculation, the long known<sup>[35]</sup> "effective medium" approximation, the description of which is beyond the scope of this review, works well (see, for example, the splendid review by Kirkpatrick<sup>[36]</sup>). We are interested here in the case when the inhomogeneity of the electric conductivity is exponentially large, i.e.,

$$\sigma(r) = \sigma_0 e^{-\xi(r)}, \quad (3.1)$$

with  $\langle (\xi(r) - \langle \xi \rangle)^2 \rangle \gg 1$ . This form is assumed, for example, by the electric conductivity of a semiconductor with large-scale fluctuations of the potential, which bend the bottom of the conduction band.<sup>[11]</sup> In this case  $\xi(r) = \epsilon(r)/T$ , where  $\epsilon(r)$  is the local value of the distance from the Fermi level to the bottom of the conduction band and  $T$  is the temperature in the energy scale.

We now present arguments that show that the determination of the exponent of the effective electric conductivity reduces to a solution of a percolation-theory problem.<sup>[11,12]</sup> We specify a certain value  $\xi$ , separate the regions of space in which  $\xi(r) \leq \xi$ , calling them (mentally) black, and call the remaining region white. We introduce a quantity  $\sigma_\xi$  defined as the effective conductivity of a medium in which the white regions are replaced by a dielectric. It is obvious that the effective conductivity  $\sigma$  of interest to us is equal to  $\lim_{\xi \rightarrow \infty} \sigma_\xi$ . At small values of  $\xi$ , the black regions form isolated islands and  $\sigma_\xi = 0$ . Starting with a certain critical value  $\xi = \xi_c$ , these regions form branched chains of interconnected lakes. At the least excess of  $\xi$  over  $\xi_c$  the density of such chains becomes finite and increases with  $\xi - \xi_c$  in power-law fashion. The resistance of this critical network is determined by the resistance of the sections with the highest resistivity. (By definition,

these sections cannot be shunted by low-resistivity sections, for otherwise percolation would set it at  $\xi < \xi_c$ .) Therefore, at  $\xi = \xi_c$  on the order of unity we have  $\sigma_\xi \approx \exp(-\xi_c)$ . (We neglect terms of order of unity in the argument of the exponential.) Further increase of  $\xi$  does not change the exponential dependence of  $\sigma_\xi$ , for in this case regions with conductivity exponentially smaller than  $\exp(-\xi_c)$  are included and are shunted by the aforementioned critical net, it follows therefore that the principal term of the logarithm of the effective conductivity is determined by the formula

$$\ln \frac{\sigma}{\sigma_0} = -\xi_c. \quad (3.2)$$

Thus, the problem of determining the principal term in the exponent of the effective conductivity has been reduced to the continual problem of percolation theory which was formulated at the end of the preceding section. If the properties of the medium are such that the electric conductivity is not a continuous function of the coordinates, then other problems of percolation theory arise. Kirkpatrick<sup>[37]</sup> undertook to check the ideas on which the foregoing derivation of (3.2) are based with the aid of the following model: We consider a simple cubic lattice, between the nearest sites of which are connected random resistors the values of which have a large scatter. We represent these resistors in the form  $R = R_0 e^\xi$  and assume that  $R_0$  is the same for all the resistors, while the random quantity  $\xi$  is uniformly distributed in the interval from  $-\ln A$  to  $\ln A$ . If  $A = 1$ , then all the resistors are equal, and the effective electric conductivity  $\sigma$  (per resistor) is equal to  $\sigma_0 = 1/R_0$ . At  $A \gg 1$  we can find  $\ln(\sigma/\sigma_0)$  by percolation theory. To this end we should mentally include all the resistors with  $\xi < \xi_c$  and choose  $\xi_c$  from the condition that percolation over the connected resistors set in. Then the result is expressed by formula (3.2). It is easy to see that in this case  $\xi_c$  is determined from the solution of the lattice bond problem. According to the results given in the table, the critical fraction of the connected resistors  $x_c(b)$  is in this case equal to 0.25. It is now easy to find  $\xi_c$ . From the conditions of the problem, the distribution function  $F$  is of the form

$$F(\xi) = \begin{cases} (2 \ln A)^{-1}, & |\xi| \leq \ln A, \\ 0, & |\xi| > \ln A. \end{cases} \quad (3.3)$$

If all the resistors with  $-\ln A < \xi < \xi_c$  are connected, then the fraction of the connected resistors is

$$x(\xi_c) = \int_{-\ln A}^{\xi_c} F(\xi) d\xi. \quad (3.4)$$

The quantity  $\xi_c$  is determined by the condition  $x(\xi_c) = 0.25$ . Calculating the integral (3.4), we obtain

$$\xi_c = -\frac{1}{2} \ln A \quad (3.5)$$

and according to (3.2) we have

$$\ln \frac{\sigma}{\sigma_0} = \frac{1}{2} \ln A. \quad (3.6)$$

The verification undertaken by Kirkpatrick consisted of numerically calculating the effective electric conductivity as a function of  $A$ . The calculation was carried out for a cube having  $15^3$  sites and simulating an infinite lattice. A computer was used to solve the system of Kirchoff's equations that express the laws of current conservation in each site. It turns out that the results obtained in Kirkpatrick's first paper<sup>[37]</sup> do not agree with (3.6), this being the reason for lack of faith in the method described in this chapter. It must be borne in mind, however, that formulas (3.2) and (3.6) are valid

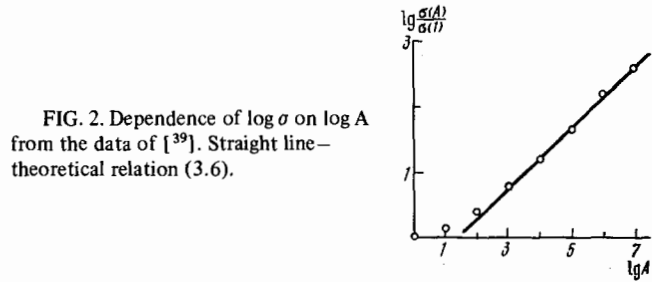


FIG. 2. Dependence of  $\log \sigma$  on  $\log A$  from the data of [39]. Straight line— theoretical relation (3.6).

only at large values of  $A$ , when  $\ln A \gg 1$ . In the first calculations Kirkpatrick succeeded in advancing only to  $A \approx 10^3$ . This turned out to be not enough. Subsequent calculations carried out both by Kirkpatrick himself<sup>[38]</sup> and by other workers<sup>[39]</sup> have shown that at sufficiently large  $A$  ( $A \geq 10^4$ ) formula (3.6) is valid with high accuracy (Fig. 2). Thus, the numerical calculations have made it possible not only to verify the percolation method, but also to refine the limits of its applicability.

#### 4. THEORY OF HOPPING CONDUCTIVITY

We now apply the ideas developed in the preceding section to construct a theory of hopping conductivity (HC). Hopping conductivity is customarily called the transport of current due to hopping of the carriers between different localized states. This type of conductivity was predicted by Gudden and Schottky<sup>[40]</sup> and observed first in silicon carbide and in germanium. Subsequently HC was observed and investigated in practically all crystalline semiconductors. In recent years HC was observed also in a large number of amorphous semiconductors, where it spans a much larger temperature interval and plays accordingly a much more important role. We shall first describe briefly the experimental facts. A more detailed exposition can be found in the reviews<sup>[17,41]</sup> and in the book<sup>[42]</sup>.

##### a) Fundamental Experimental Data

We start with crystalline semiconductors. At room temperatures and lower, the conductivity of most semiconductors is due to the presence of impurities that produce local levels in the forbidden band. An individual impurity atom can be characterized by an ionization energy  $A_0$  and by the distance  $a$  over which the wave function of the localized impurity state falls off. If the impurity concentration  $N$  is not very large, so that  $Na^3 \ll 1$ , then the impurity states overlap little and retain their individuality. Conduction in such weakly doped semiconductors at relatively high temperatures is effected by carriers that are thermally thrown from the impurity levels to the allowed bands. With decreasing temperature, the concentration of the electrons in the conduction band becomes so low (for the sake of argument, we speak of an n-type semiconductor) that the hopping of the electrons directly between the donors, which is due to the small but finite overlap of the wave functions of neighboring impurities, begins to make a large contribution to the current. The transition from allowed-band conductivity to the HC with decreasing temperature can be clearly seen in Fig. 3, which shows the temperature dependence of the resistivity of germanium<sup>[43]</sup>; such a dependence is typical of all weakly-doped semiconductors. In the HC region, the electric conductance takes the form

$$\sigma = \sigma_3 \exp\left(-\frac{e_3}{T}\right). \quad (4.1)$$

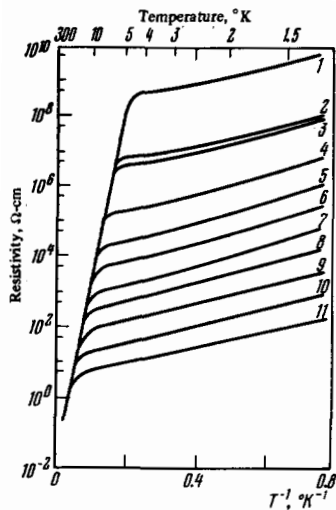


FIG. 3. Dependence of the resistivity on the temperature for p-type Ge with degree of compensation  $K = 0.4$ .<sup>[43]</sup> The concentration of the acceptors in samples 1 to 11 is equal to (in  $\text{cm}^{-2}$ ): 1- $7.5 \cdot 10^{14}$ , 2- $1.4 \cdot 10^{15}$ , 3- $1.5 \cdot 10^{15}$ , 4- $2.66 \cdot 10^{15}$ , 5- $3.6 \cdot 10^{15}$ , 6- $4.8 \cdot 10^{15}$ , 7- $7.2 \cdot 10^{15}$ , 8- $9.0 \cdot 10^{15}$ , 9- $1.4 \cdot 10^{16}$ , 10- $2.4 \cdot 10^{16}$ , 11- $3.5 \cdot 10^{16}$

The subscript "3" is customarily used to describe HC of weakly-doped semiconductors.<sup>[41]</sup>

The necessary condition for HC is the presence of free places on the donors. At low temperatures, it can be ensured only by compensation of the semiconductor, i.e., by the presence of a certain concentration of minority carriers. For example, acceptors in an n-type semiconductor capture part of the electrons from the donors and become negatively charged. The result is the same number of empty (positively charged) donors. The role of compensation is not limited to this, however. The charged donors and acceptors resulting from the compensation produce by means of their random potential a scatter of the donor levels, which greatly exceeds the exponentially small splitting of the levels of the neighboring donors due to the overlap of the wave functions. This prevents a quantum "smearing" of the electron over the donors and leads to localization of the states corresponding to individual donors.<sup>[2]</sup> Owing to the scatter of the levels, the transition of the electron from one donor to another is possible only with absorption and emission of phonons. Therefore HC, just like the band conductivity of a weakly-doped semiconductor, has an activation-type temperature dependence.

Figure 3 shows one more characteristic feature of HC, namely the exceptionally strong dependence of  $\sigma_3$  on the impurity concentration. The physical cause of this phenomenon is that with decreasing concentration the distances between the donors increase, and the probabilities of the hops between the neighboring donors decrease exponentially.

A large body of experimental data has been accumulated by now on the dependences of  $\sigma_3$  and  $\epsilon_3$  on the concentration, degree of compensation, the chemical nature of the impurities, the deformation, and the magnetic field.<sup>[17,41]</sup>

There is much less known concerning the electronic states of amorphous semiconductors than of crystalline semiconductors. These states are connected not with the impurities but with the fluctuations of the structure or of the stoichiometric composition. The state density near the Fermi level, which is located in the center of the forbidden band, is small enough for the states to be localized.

The temperature dependence of the HC of amorphous semiconductors<sup>[44]</sup> differs from (4.1) and apparently

agrees with good accuracy with the relation

$$\sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/4} \right] \quad (4.2)$$

proposed by Mott.<sup>[45]</sup> This difference, however, is connected not with the qualitative singularities of the electron states, but with a pure quantitative difference between the energy and spatial scales in both cases. A confirmation of this point of view is the fact that in weakly-doped semiconductors, too, at infralow temperatures  $T < 1^\circ\text{K}$ , the law (4.1) gives way to a relation of the type (4.2).<sup>[46-48]</sup> We shall show below that a single method, based on percolation theory, makes it possible to obtain in different temperature intervals both the constant-activation-energy regime (4.1) and Mott's law (4.2).

## b) Random Network of Resistors

An important contribution to the theory of HC was made by Miller and Abrahams.<sup>[13]</sup> They have shown that the problem can be reduced to a calculation of the conductivity of a random network of resistors, each connected with the hopping between a definite pair of donors. The simplest and most general proof of the analogy with a network of resistors is contained in<sup>[12]</sup>. We trace below only briefly the manner in which the problem is reduced to this equivalent circuit.

Consider two donors numbered  $i$  and  $j$ , located at the points  $\mathbf{r}_i$  and  $\mathbf{r}_j$  and having energies  $\epsilon_i$  and  $\epsilon_j$ . The energy difference  $|\epsilon_i - \epsilon_j|$  in typical semiconductors is much smaller than the Debye temperature. The hopping processes proceed with absorption or emission of one phonon. Let the electron spectrum be isotropic, so that the wave function of the donor takes the form

$$\psi_j(r) = \pi^{-1/2} a^{-3/2} \exp \left( - \frac{|r - \mathbf{r}_j|}{a} \right). \quad (4.3)$$

Then calculation in first-order perturbation theory in terms of the deformation interaction of the longitudinal acoustic phonons with the electrons yields for the number of transitions between the donors  $i$  and  $j$  per unit time

$$\Gamma_{ij} = \gamma_{ij} e^{-2r_{ij}/a} f_i (1 - f_j) \begin{cases} \mathcal{N}(e_j - \epsilon_i) & (\text{absorption}) \\ \mathcal{N}(\epsilon_i - e_j) + 1 & (\text{emission}) \end{cases} \quad (4.4)$$

where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ , the factor  $\exp(-2r_{ij}/a)$  is connected with the overlap of the wave functions of the electrons at the impurities  $i$  and  $j$ ,  $\mathcal{N}(\epsilon)$  is the Planck function, and  $f_i$  is the occupation function of the state  $i$ . The factor  $\gamma_{ij}$  depends in power-law fashion on  $r_{ij}$  and  $\epsilon_i - \epsilon_j$ . Its explicit form is given in<sup>[13]</sup>. Under equilibrium we have

$$f_i = f^0(e_i) = \left[ 1 + \frac{1}{2} \exp \left( \frac{e_i - \mu}{T} \right) \right]^{-1}, \quad (4.5)$$

where  $\mu$  is the chemical potential. The frequencies of the transitions  $i \rightarrow j$  and  $j \rightarrow i$  are in this case equal to each other and there is no current. The electric field leads to two changes in  $\Gamma_{ij}$ . First, the field changes the energies of the donor states and consequently the energy of the phonon that takes part in the hopping. In a weak electric field  $\mathbf{E}$ , the phonon system remains in equilibrium. Therefore, the first change reduces to addition of a term  $e\mathbf{E} \cdot \mathbf{r}_{ij}$  to the argument of the Planck function. The second change consists in the fact that the field redistributes the electrons over the donors, i.e., it adds increments  $\delta f_i$  to the functions (4.5). We write these increments in the form

$$f_i(e) = f^0(e_i) + \delta f_i = \left[ 1 + \frac{1}{2} \exp \left( \frac{e_i - \delta \mu_i - \mu}{T} \right) \right]^{-1}. \quad (4.6)$$

If we substitute (4.6) in (4.4) and take into account the changes in the arguments of the Planck functions, then the balance between the transitions  $i \rightarrow j$  and  $j \rightarrow i$  is upset, and a current will flow between the donors  $i$  and  $j$ . In the approximation linear in  $E$  and  $\delta\mu$ , direct calculation leads to the following expression for the excess number of electrons that goes over per unit time from donor  $i$  to donor  $j$ :

$$\Gamma_{ij}(E) - \Gamma_{ji}(E) = \frac{\Gamma_{ij}^0}{T} (eE r_{ij} + \delta\mu_i - \delta\mu_j), \quad (4.7)$$

where  $\Gamma_{ij}^0$  is the frequency of the transitions  $i \rightleftharpoons j$  at equilibrium. The factor in the parentheses in (4.7) can be regarded as the difference between the electrochemical potentials between the donors  $i$  and  $j$ . Then the quantity

$$R_{ij} = \frac{T}{e^2 \Gamma_{ij}^0} \quad (4.8)$$

can be naturally interpreted as a resistance connected between the donors  $i$  and  $j$ . Substituting the equilibrium distribution function in (4.7) and (4.8) at  $T \ll |\epsilon_i - \mu|$ , we write  $R_{ij}$  in the form

$$R_{ij} = R_{ij}^{(0)} \exp \xi_{ij}, \quad (4.9)$$

where

$$\xi_{ij} = \frac{2r_{ij}}{a} + \frac{e_{ij}}{T}, \quad (4.10)$$

$$R_{ij}^{(0)} = \frac{T}{e^2 \Gamma_{ij}^0}, \quad (4.11)$$

$$\epsilon_{ij} = \frac{1}{2} (|\epsilon_i - \mu| + |\epsilon_j - \mu| + |\epsilon_i - \epsilon_j|). \quad (4.12)$$

We have thus obtained a network of resistors  $R_{ij}$  which connect randomly disposed sites (impurities). The quantities  $\delta\mu_i$  must be obtained from the condition that the incoming and outgoing currents be equal at each site (Kirchoff's first law) and from the condition that the sum of the electrochemical potentials in any closed circuit be equal to the voltage applied to this circuit (Kirchoff's second law).

An important feature of the considered network is the unusually broad spectrum of the values of  $R_{ij}$ . Indeed, in the situation typical of experiments with weakly-doped semiconductors, the average distance between impurities  $N^{-1/3}$  amounts to from 6 to 12 Bohr radii  $a$ . The resistances of the pair with  $r_{ij} = N^{-1/3}$  and the pair with  $r_{ij} = 2N^{-1/3}$  differ by factor  $e^{12-24}$ . A strong scatter at sufficiently low temperatures results also from the energy term (4.10). Thus, the considered network is an ideal object for the application of the percolation method described in Chap. 3. In accordance with this method, to find the conductivity exponent we shall first imagine that all the resistors are disconnected. We then connect all the resistors with  $\xi_{ij} < \xi$  and increase  $\xi$  until percolation over the connected resistors sets in. If the threshold value is  $\xi_c$ , then

$$\sigma = \sigma_0 \exp(-\xi_c). \quad (4.13)$$

To find  $\xi_c$  it is obviously necessary to solve the following percolation-theory problem. We are given random points (sites) with concentration  $N$  and with given distribution of the energies  $\epsilon_i$ . Two points are regarded as bound if

$$\xi_{ij} = \frac{2r_{ij}}{a} + \frac{e_{ij}}{T} \leq \xi. \quad (4.14)$$

It is required to find the threshold value of  $\xi$  at which the bound points first form an infinite cluster. This problem is a particular case of the third class of percolation-theory problems—random-site problems. In

the general case, the left-hand side of the binding criterion (4.14) can be an arbitrary function of  $r_i$ ,  $r_j$ ,  $\epsilon_i$ , and  $\epsilon_j$  and can depend not only on these but also on other characteristic sites. We shall see that problems of this class play an exclusive role in the theory of HC.

### c) Concentration Dependence of the Hopping Conductivity

As mentioned in Sec. (a), the exponential dependence of the HC on the concentration is contained in the quantity  $\sigma_3$ . To calculate it we must consider temperatures at which the characteristic values  $\epsilon_{ij}/T < 1$ . Then the binding criterion takes the form

$$r_{ij} \leq \frac{\xi_c}{2} \equiv r, \quad (4.15)$$

i.e., the given site is bound with all the sites lying inside a sphere of radius  $r$  around it. At a certain threshold value  $r_c$  of the parameter  $r$ , there arise for the first time infinite sequences of sites in which each succeeding site lies inside the sphere around the preceding one. According to (4.15),

$$\xi_c = \frac{2r_c}{a} \quad (4.16)$$

and consequently

$$\sigma_3 = \sigma_0 e^{-2r_c/a}. \quad (4.17)$$

As we have seen with p-Ge as an example (see Fig. 3), the concentration dependence of  $\sigma_3$  is particularly clearly pronounced, so that the question of the percolation radius  $r_c$  is pertinent. The quantity  $r_c$  was calculated many times and quite carefully<sup>[5,49-58]</sup>. The results of different workers are compared in<sup>[54]</sup>. According to<sup>[54]</sup>

$$r_c = (0.87 \pm 0.04) N^{-1/3}. \quad (4.18)$$

If the results<sup>[53,55]</sup> are extrapolated to an infinite block in accordance with the law obtained in<sup>[54]</sup>, then they turn out to be close to (4.18). Substitution of (4.18) and (4.17) yields

$$\sigma_3 = \sigma_0 \exp\left(-\frac{\alpha N^{-1/3}}{a}\right), \quad (4.19)$$

where  $\alpha = 1.74 \pm 0.02$ . The result (4.19) was verified directly by computer solution of the system of Kirchoff's equations for a random network with resistances  $R_{ij} = R_0 \exp(2r_{ij}/a)$ .<sup>[39]</sup> The calculated dependence of the resistivity of the network on the impurity concentration agrees well with formula (4.19).

A reduction of the experimental data given for p-Ge in Fig. 4 shows that  $\ln \sigma_3$  is a linear function of  $N^{-1/3}$ . The slope of the line makes it possible to determine  $\alpha$  from the known value of the Bohr radius of the acceptor. According to<sup>[17]</sup>,  $\alpha = 1.9 \pm 0.1$ . The same value (but with an uncertainty  $\sim 0.2$ ) is obtained by a reduction of the data of p-Si and n-GaAs.<sup>[17,57]</sup> The slight excess of

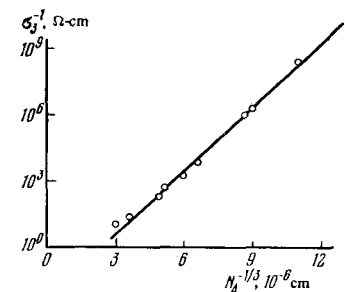


FIG. 4. Conductivity  $\sigma_3$  of p-germanium with gallium impurity as a function of the gallium concentration in accordance with the data of<sup>[43]</sup>. The degree of compensation of all the samples is  $K = 0.4$ .

the experimental value over the theoretical one can be attributed in principle to the small correlation in the impurity positions, due to their repulsion in the melt.

In the aforementioned experiments, the wave function of the impurity far from the center agrees with good accuracy with (4.3). In many semiconductors, however, for example n-Ge and n-Si, the wave functions of the impurities are strongly anisotropic. A strong anisotropy can be intentionally produced by a strong magnetic field or by uniaxial deformation in the investigation of the effects of the magnetoresistance and piezoresistance in semiconductors with initially isotropic wave functions.

In the case of anisotropic wave functions  $\psi_1(\mathbf{r})$ , the term  $2r_{ij}/a$  and  $\xi_{ij}$  is replaced by the complicated function  $\varphi(r_{ij})$ , which coincides with the argument of the exponential of the quantity  $|\int \psi_1 \psi_j d^3r|^2$ . To find  $\sigma_3$  it is now necessary to solve the percolation-theory problem with the binding criterion

$$\varphi(r_{ij}) \leq \xi, \quad (4.20)$$

which is satisfied when  $r_{ij}$  lies not inside a sphere but inside a closed surface  $S_\xi$  of more complicated shape. The volume  $V_\xi$  bounded by the surface  $S_\xi$  increases with increasing parameter  $\xi$ . It is necessary to find the critical value  $\xi = \xi_c$  at which the IC of the bound sites first occurs. The value of  $\sigma_3$  is determined as before by formula (4.13).

The percolation threshold  $\xi_c$  is conveniently characterized by the average number of bonds  $B_c = NV_{\xi_c}$  emerging from one site. An analogous quantity  $\tilde{B}_c = (4\pi/3)Nr_c^3 \approx 2.8$  can be introduced also for the sphere problems (4.15). The quantity  $B_c$  can in principle depend on the shape of the surface  $S_\xi$ . In<sup>[17,58]</sup> it was proved that the values of  $B_c$  are the same for all the surfaces obtained from one another by a linear transformation of the coordinates, for example, for a sphere and any ellipsoid. In<sup>[63]</sup> the values of  $B_c$  were calculated by the Monte Carlo method for the surfaces that are essential in the applications described below and for a number of other surfaces. It turned out that for convex surfaces (including a sphere) the values of  $B_c$  are the same within 3%, i.e.,  $B_c$  is approximately an invariant analogous to  $zxc(b)$  in the bond problem. Calculations for concave surfaces seem to indicate that  $B_c$  seems to decrease with the degree of concavity, but not more than by 10–20%.

Let us consider the main applications of the percolation method for anisotropic impurity wave functions. In<sup>[53]</sup> the method was used to describe the concentration dependence of  $\sigma_3$  for n-Ge, where  $S_\xi$  is the surface enveloping four intersecting oblate ellipsoids of revolution, the axes of which are directed along (111).  $B_c$  was calculated for this surface, and this made possible a comparison with experiment. In<sup>[17,53]</sup> the concentration dependence of  $\sigma_3$  was calculated for uniaxially deformed n-Ge and p-Ge. This dependence arises because of a restructuring of the electron spectrum under the influence of the deformation and a change in the form and volume of the wave function. For both deformed and undeformed germanium, the calculation method leads to satisfactory agreement with the experimental data.<sup>1)</sup>

<sup>1)</sup>We take the opportunity to correct an error that has crept in the plots of  $\ln \sigma_3$  against  $N^{-1/3}$  for germanium with antimony and phosphorus impurities. [17,59] From the initial experimental data [59,60] it follows that  $\ln \sigma_3 = (-3 + 0.1) \cdot 10^6 (\text{cm}^{-1}) N^{-1/3}$  for antimony and  $\ln \sigma_3 = -(3.6 \pm 0.2) \cdot 10^6 (\text{cm}^{-1}) N^{-1/3}$  for phosphorus, in place of the relations given in [53].

#### d) Theory of Hopping Magnetoresistance

The most interesting and productive is the application of the percolation method for anisotropic wave functions to the theory of giant magnetoresistance.<sup>[58,61]</sup> It is well known that a strong magnetic field constricts the wave functions of the impurity electrons in the transverse direction, transforming them in the simplest case from spherically-symmetrical into cigar-shaped. The overlap of the "tails" of the wave functions of the neighboring impurities decreases sharply, on the average, and this leads to an exponential increase of the hopping resistance. An exponentially large positive magnetoresistance was observed in n-InSb<sup>[62]</sup>, n-Ge<sup>[63]</sup>, p-Ge<sup>[64,65]</sup>, n-InP<sup>[66]</sup>, n-GaAs<sup>[67,68]</sup>. An increase of the resistance by  $10^5$  times was reached in<sup>[62,67]</sup> in the maximum magnetic fields 28 kOe and 140 kOe, respectively. The theory starts from expressions for the "tails" of the wave functions of a hydrogenlike center in a magnetic field. At relatively short distances from the center  $r < \lambda^2/a$  ( $\lambda = \sqrt{ch/eH}$  is the magnetic length) the exponent of the wave function acquires a term that is small in comparison with the main term

$$\psi(r) \sim \exp\left(-\frac{r}{a} - \frac{r^2 a \sin^2 \varphi}{24\lambda^2}\right), \quad (4.21)$$

where  $\varphi$  is the angle between the vector  $\mathbf{r}$  and the  $z$  axis, which coincides with the direction of the magnetic field (the nucleus is at the origin). At large distances  $r > \lambda^2/a$ , the magnetic field changes completely the exponent of the wave function

$$\psi(r) \sim \exp\left(-\frac{|z|}{a_H} - \frac{x^2 + y^2}{4\lambda^2}\right), \quad (4.22)$$

where  $a_H = [2mE(H)]^{-1/2} \hbar$ ,  $m$  is the effective mass, and  $E(H)$  is the binding energy of the hydrogenlike center with the magnetic field  $H$ . Which of the formulas, (4.21) or (4.22), should be used for the calculation of the overlap integral depends on the ratio of the average distance between impurities  $N^{-1/3}$  and the value of  $\lambda^2/a$ . At a given impurity concentration, formulas (4.21) are valid in relatively weak fields ( $H < H_c \equiv N^{1/3} ch/ea$ ), and formula (4.22) is valid in strong fields ( $H > H_c$ ). With the aid of (4.21) and (4.22) one calculates the function  $\varphi(r_{ij})$  (the exponent of the quantity  $|\int \psi_1 \psi_j d^3r|^2$ ), which enters in the binding criterion. At  $H < H_c$  the surface  $S_\xi$  is an ellipsoid of a revolution that is slightly prolate along the  $z$  axis. In strong fields,  $S_\xi$  constitutes two identical truncated paraboloids of revolution with the bases flush in contact. As already mentioned above,  $B_c \approx 2.8$  for these surfaces. Calculating in each case the volume  $V(\xi, H)$  of the surface, we obtain  $\xi_c$  from the condition  $NV(\xi_c, H) = B_c$  and substituting  $\xi_c$  in (4.13) we obtain<sup>[58,61]</sup>

$$\sigma_3(H) = \sigma_3(0) \exp\left(-0.04 \frac{ae^3}{Nc^2 \hbar^2} H^2\right) \quad (H < H_c), \quad (4.23)$$

$$\sigma_3(H) \sim \exp[-0.95 (Na_H \lambda^{-1/2})] \quad (H > H_c). \quad (4.24)$$

In the limit of very strong magnetic fields, when  $E(H) = E_0 \ln^2(a/\lambda)^2$ , formula (4.24) yields

$$\sigma_3 \sim \exp(-\text{const} \cdot \sqrt{H} \sqrt{\ln H}) \quad (4.25)$$

The degree of agreement of (4.23)–(4.25) with the experimental data can on the whole be regarded as satisfactory.<sup>[17,58]</sup>

A result similar to (4.23) was obtained by Mikošhiba.<sup>[69]</sup> However, owing to the rough calculations made in the determination of the wave functions and owing to the absence of an averaging procedure based on percolation considerations, the numerical coefficient



in the exponential obtained by Mikoshiba is twice that in (4.23).

It is interesting to note that the results (4.23)–(4.25) pertain equally well to transverse and longitudinal magnetoresistance. At first glance this may appear paradoxical. After all, the wave functions of the impurities in the magnetic field are strongly elongated along the field and the probability of hopping through a specified distance in longitudinal direction exceeds exponentially the probability of hopping in the transverse direction. If we use chains consisting of longitudinal hops for the longitudinal conduction and consisting of transverse hops for the transverse conduction, then the exponential difference should remain also in the expression for the conductivity. From the premises of the percolation method, however, it follows that inasmuch as a cluster that is infinite in all directions is produced beyond the percolation threshold the electric conductivity of this cluster in all directions is determined by the same resistances with  $\xi_{ij} = \xi_c$ . This conclusion is in good agreement with the results of Sladek<sup>[62]</sup>, who observed in n-InSb an increase in the resistance by  $10^5$  times at a two- to threefold difference between the longitudinal and transverse effects. The character of the longitudinal and transverse electric conductivity is considered in greater detail in<sup>[17]</sup>.

### e) Temperature Dependence of the Hopping Conductivity

In this section we shall show how to determine, with the aid of a specified distribution of the energy levels, the exponential temperature dependence of the hopping conductivity. In accordance with the general prescription described in Sec. (b), it is necessary for this purpose to find the value of  $\xi_c$ , taking into account the quantities  $\epsilon_{ij}/T$  in the binding condition (4.14). We shall show below that if the temperature and the distribution function of  $\epsilon_{ij}$  are such that for neighboring impurities we have

$$\frac{\epsilon_{ij}}{T} \ll \frac{2r_{ij}}{a} \quad (4.26)$$

then the temperature dependence of the conductivity takes the form (4.1). Following<sup>[70]</sup>, we present a prescription for finding the activation energy  $\epsilon_3$  in this case. If the inequality (4.26) is not satisfied and the density of states near the Fermi level can be regarded as independent of the energy, then Mott's law (4.2) holds. When the density of states near the Fermi level has a power-law variation, the exponent (4.2) takes a different form.<sup>[14,70-72]</sup>

We start with the case when the inequality (4.14) is satisfied. Under these conditions, the term  $\epsilon_{ij}/T$  in (4.14) adds to  $\xi_c$  an increment that is relatively small, but is responsible for the entire exponential temperature dependence of the electric conductivity.

Before we proceed to determine this increment, let us discuss the statistical properties of  $\epsilon_{ij}$ . The simplest situation is one in which the energies  $\epsilon_i$  for different sites are independent and are distributed in like fashion. In this case, although the distribution of  $\epsilon_{ij}$  is the same for all pairs, the values of  $\epsilon_{ij}$  and  $\epsilon_{jk}$  for two pairs having a common site turn out to be correlated in accordance with (4.12). More realistic is the situation in which the energies  $\epsilon_i$  and  $\epsilon_j$  are correlated, and the degree of correlation depends on the distance  $r_{ij}$ . The characteristic distance up to which cor-

relation takes place will be called the correlation length  $r_0$ . Owing to the correlation of the energies, the distribution function of  $\epsilon_{ij}$  turns out to be different for a pair with different distances  $r_{ij}$ , and the values of  $\epsilon_{ij}$  turn out to be correlated for pairs that are not far enough from each other.

Having in mind to return to a real situation, we consider first a hypothetical case, when the distributions of  $\epsilon_{ij}$  for all pairs are identical and independent. In this case the quantity  $\xi_c$  is determined entirely by the distribution function of  $\epsilon_{ij}$ . The analysis that follows is based on the assumption that  $\xi_c$  can be expanded in the moments of the distribution function

$$\frac{\xi_c}{\xi_c^0} = 1 + A \frac{\langle \epsilon_{ij} \rangle}{\xi_c^0 T} + B \left\langle \left( \frac{\epsilon_{ij}}{\xi_c^0 T} \right)^2 \right\rangle + c \left\langle \left( \frac{\epsilon_{ij}}{\xi_c^0 T} \right) \right\rangle^2, \quad (4.27)$$

where the symbol  $\langle \dots \rangle$  denotes averaging. To determine the coefficient  $A$ , we assume that all the  $\epsilon_{ij}$  are identical and equal to  $\epsilon'$ . Then, neglecting the terms of (4.27), that are quadratic in  $\epsilon_{ij}/T$ , we obtain  $\xi_c = \xi_c^0 + A(\epsilon'/T)$ . On the other hand, from the definition of  $\xi_c$  it is directly obvious that in this case  $\xi_c = \xi_c^0 + (\epsilon'/T)$ . Consequently,  $A = 1$  and for an arbitrary distribution function formula (4.27) assumes, accurate to the linear terms, the form  $\xi_c = \xi_c^0 + \langle (\epsilon_{ij}) \rangle / T$ . According to (4.13) this means that

$$\epsilon_3 = \langle \epsilon_{ij} \rangle. \quad (4.28)$$

We shall show now that the perturbation-theory method described above is applicable also to the more complicated situation when  $\langle \epsilon_{ij} \rangle$  depends on  $r_{ij}$  and the values of  $\epsilon_{ij}$  belonging to different sites are correlated. We note first that introduction of the small term  $\epsilon_{ij}/T$  in (4.14) violates the condition of the binding of the sites only the quantity  $2r_{ij}/a$  is very close to  $\xi_c^0$ , i.e.,  $r_{ij} \approx r_c$ . Pairs with this value of  $r_{ij}$  are rare and are located at large distances from one another. In Sec. (f) we shall present arguments to show that only a negligible fraction of these pairs plays an important role in percolation.

This leads to two important conclusions. First, in the perturbation theory proposed above the quantities  $\epsilon_{ij}$  can be regarded as uncorrelated also at finite values of the correlation length  $r_0$ . All that matters is that  $r_0$  must be smaller than the distance between the points that are important in the percolation. Second, if the quantity  $\langle \epsilon_{ij} \rangle$  depends on  $r_{ij}$  in this case then it is possible, in analogy with (4.27), to expand  $\xi_c$  in the moments of the distribution function of the quantities  $\epsilon_{ij}$  at  $r_{ij} = r_c$ . As a result we obtain

$$\epsilon_3 = \langle \epsilon_{ij} \rangle_{r_{ij}=r_c}. \quad (4.29)$$

Formula (4.29) was verified with a computer by the Monte Carlo method in<sup>[70]</sup>.

We consider now another case, when an inequality inverse to (4.26) holds for neighboring sites. In this case the resistors connecting the neighboring sites are determined by the factor  $\exp(\epsilon_{ij}/T)$ . At the same time, among the pairs of sites with sufficiently large distance  $r_{ij}$  one can always find such pairs for which the energies  $\epsilon_i$  and  $\epsilon_j$  are close to the Fermi level and the values of  $\epsilon_{ij}$  are small. For these pairs, the contribution of the term  $\epsilon_{ij}/T$  to  $\xi_{ij}$  decreases, but the term  $2r_{ij}/a$  increases. Owing to the competition between these terms, the optimal hops are those for which both terms are of the same order of magnitude. These considerations are due to Mott<sup>[45]</sup>, who obtained the char-

acteristic length of the optimal hops and obtained the law (4.2), which bears his name.

A rigorous derivation of (4.2) on the basis of percolation theory was obtained by Ambegaokar et al.<sup>[12]</sup> We proceed to describe this derivation. We introduce the maximum values of  $\epsilon_{ij}$  and of the distance  $r_{ij}$  that are permitted by the binding condition (4.14),

$$r_{\max} = \frac{a\xi_c}{2}, \quad \epsilon_{\max} = T\xi_c. \quad (4.30)$$

To satisfy (4.14) it is necessary (but not sufficient) that neither  $|\epsilon_i - \mu|$  nor  $|\epsilon_j - \mu|$  exceed  $\epsilon_{\max}$ . The derivation of Mott's law is based on the important assumption that the density of states  $g(\epsilon)$  can be regarded as a constant in an energy interval on the order of  $\epsilon_{\max}$  on either side of the Fermi level. In this case the concentration of the sites that fall in the band  $|\epsilon_i - \mu| \leq \epsilon_{\max}$  can be written in the form

$$n = 2g(\mu)\epsilon_{\max}. \quad (4.31)$$

We introduce now the dimensionless variables

$$s_i = \frac{r_i}{r_{\max}}, \quad \Delta_i = \frac{\epsilon_i - \mu}{\epsilon_{\max}}. \quad (4.32)$$

Then the binding condition (4.14) takes the form

$$s_{ij} + \Delta_{ij} \ll 1, \quad (4.33)$$

where

$$s_{ij} = |s_i - s_j| = \frac{r_{ij}}{r_{\max}}, \quad \Delta_{ij} = \frac{1}{2} \{ |\Delta_i| + |\Delta_j| + |\Delta_i - \Delta_j| \} = \frac{\epsilon_{ij}}{\epsilon_{\max}}. \quad (4.34)$$

The concentration of the sites in dimensionless  $s$ -space in the energy strip  $|\Delta_i| < 1$  is equal to

$$\mathcal{N} = 2g(\mu)\epsilon_{\max}r_{\max}^3 = \frac{1}{4}g(\mu)\xi_c^3 T. \quad (4.35)$$

To find  $\xi_c$  it is necessary to determine the dimensionless threshold concentration  $\mathcal{N}_C$  at which percolation sets in for the first time in a system of randomly distributed sites having energies  $\epsilon_i$  that are randomly distributed in the interval from  $-1$  to  $+1$  and with the binding criterion (4.33). Inasmuch as conditions of the problems do not contain any parameters,  $\mathcal{N}_C$  should be of the order of unity. Expressing  $\xi_c$  in terms of  $\mathcal{N}_C$  with the aid of (4.35), we obtain

$$\xi_c = \left( \frac{4\mathcal{N}_C}{g(\mu)T} \right)^{1/3}. \quad (4.36)$$

Substitution of  $\xi_c$  in (4.13) leads to formula (4.2) with the value

$$T_0 = \frac{4\mathcal{N}_C}{g(\mu)\alpha^3}. \quad (4.37)$$

In<sup>[12]</sup> there is given only the estimate  $\mathcal{N}_C = 4$ . Other estimates<sup>[14,73]</sup> of  $\mathcal{N}_C$  range from 2 to 7. To determine  $\mathcal{N}_C$ , the percolation-theory problem formulated above was solved by the Monte Carlo method in<sup>[74]</sup>. The average value of  $\mathcal{N}_C$  for 10 different realizations of random quantities turn out to be  $5.7 \pm 0.3$ . No extrapolation to an infinite bulk was made. If the extrapolation is carried out with the aid of the law proposed in<sup>[64]</sup>, then the result is  $\mathcal{N}_C = 5.3 \pm 0.3$ .

In addition to the assumption that the density of states be constant, one uses also in the derivation of Mott's law the assumption that there is no correlation between the energies of sites located in the strip  $|\epsilon_i - \mu| < \epsilon_{\max}$ . This is possible in the case when the characteristic distance between these sites  $r_{\max} = a\xi_c/2 = a(4\mathcal{N}_C/g(\mu)Ta^3)^{1/4}$  exceeds the correlation length  $r_0$  of the site energies  $\epsilon_i$ . If  $r_0 \gg N^{-1/3}$ , then a temperature interval with a different temperature de-

pendence can exist between the regions of applicability of (4.1) and (4.2) (see, e.g.,<sup>[75]</sup>).

## f) Activation Energy of Weakly-Doped Semiconductors

In this section we use the general prescription for the calculation the activation energy (4.29) in a concrete physical system—a weakly-doped compensated semiconductor. To this end it is necessary to study first the distribution of the electronic states over the energies and to find the position of the Fermi level at low temperatures. For the sake of argument we consider an n-type semiconductor. At low temperatures, each acceptor receives an electron from a donor and is charged negatively. The donor, giving up an electron, is positively charged. In a weakly-doped semiconductor it is these randomly disposed impurities which cause the main energy scatter of the electronic states. It is very important that the charged acceptors cannot change location, while the charged donor can become neutral (and vice-versa) as a result of electron hopping between the donors. At  $T = 0$  the configuration of the charged donors corresponds to the ground state of the system, calculated with allowance for the interaction of the donor electrons with one another and with the acceptors. Therefore the calculation of the density of states  $g(\epsilon)$  and of the Fermi level  $\mu$  is a very complicated many-electron problem. At comparable donor ( $N_D$ ) and acceptor ( $N_A$ ) concentrations this problem has no small parameter and cannot be solved analytically. However, solutions do exist in the cases of weak ( $K \equiv N_A/N_D \ll 1$ ) and strong ( $1 - K \ll 1$ ) compensation.<sup>[11,76]</sup> At  $K \ll 1$  almost all the donor states are occupied, and at  $1 - K \ll 1$ , to the contrary, all the states whose levels are greatly lowered by the potential of the charged impurities are occupied. Therefore the Fermi level lies above the level of the isolated impurity at  $K \ll 1$  and below this level at  $1 - K \ll 1$  (see Fig. 5). Taking the level of the isolated impurity to be the zero of the energy, we can state that with increasing  $K$  the value of  $\mu$  decreases and reverses sign at a certain intermediate compensation. At weak compensation  $K \ll 1$  the number of acceptors and charged donors is small, and the charged donors are located near the acceptors, so that the acceptor potential repels the electrons. Most acceptors have near them one ionized donor, since the potential of this donor weakens the action of the acceptor and makes it difficult to ionize the second donor. By virtue of the random character of the distribution of the impurities, however the nearest donors of certain acceptors are located so far that ionization of two donors at other acceptors becomes energywise more

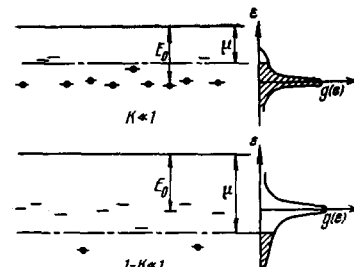


FIG. 5. Energy schemes of weakly and strongly compensated semiconductors, neglecting the large-scale potential relief. Solid line—conduction band, dash-dot—Fermi level. The short dashes show the donor levels, and dark circles show the electrons occupying them. On the right is shown the density of states at the donor levels. The occupied states are shaded. The valence band and the acceptor levels are not shown.

avored. The Fermi level is determined from the condition that the total number of ionized donors is equal to the number of acceptors, i.e., the number of acceptors ionizing two donors is equal to the number of acceptors that do not even ionize even one donor (it is shown in<sup>[76]</sup> that ionization of three donors by one acceptor is impossible at  $K \ll 1$ ). A rather complicated calculation of the number of acceptors of both types leads to the value

$$\epsilon_D = \frac{e^2}{\kappa} \left( \frac{4\pi N_D}{3} \right)^{1/3}. \quad (4.38)$$

In the case of strong compensation ( $1 - K \ll 1$ ) the electrons are at the deepest levels that are produced as a result of the close (and consequently of low probability) approach of two or several donors. For example, if there is a pair of donors at a distance  $r$  ( $a \ll r \ll N_D^{1/3}$ ), then the energy of the single electron in the pair is decreased by an amount  $e^2/\kappa r$ . If level shifts that are small in comparison with the Bohr energy  $E_0$  are investigated, then the main contribution to the density of states is made precisely by pairs<sup>[11]</sup> (and not by groups of three or four). Simple calculation of the number of pairs producing levels in a given interval makes it possible to determine the density of states at large negative energies and to find the Fermi level<sup>[11]</sup>

$$g(\epsilon) = \frac{2\pi N_D^2 e^6}{e^4 \kappa^3}, \quad \mu = -\frac{e_D}{2^{1/3}(1-K)^{1/3}}. \quad (4.39)$$

An important feature of the cases of strong and weak compensation is that the Fermi level is in the tail and is far from the peak of the density of states, at a distance much larger than the half-width of the peak (see Fig. 5). For this reason, for an overwhelming majority of the resistors of the network, it is possible to neglect the energies  $\epsilon_i$  and  $\epsilon_j$  in comparison with  $\mu$  in expression (4.12) for  $\epsilon_{ij}$ . Therefore the use of formula (4.29) yields for the activation energy

$$\epsilon_s = |\mu| \quad (4.40)$$

or, according to (4.38) and (4.39)

$$\epsilon_s = 0.61 e_D \quad \text{if } K \ll 1, \quad (4.41)$$

$$\epsilon_s = 2^{-1/3} e_D (1-K)^{-1/3} \quad \text{if } 1-K \ll 1. \quad (4.42)$$

The result (4.40) can be illustratively interpreted. The concentration of the electrons (at  $1 - K \ll 1$ ) or of the vacancies (at  $K \ll 1$ ) thrown from the Fermi level to the peak of the density of states is proportional to  $e^{-|\mu|T}$ , and the mobility due to hopping between the states belonging to the peak depends little on the temperature. Therefore the conductivity activation energy coincides with the value of  $|\mu|$ .

So far we have spoken of shifts of the donor levels due to their nearest environment. Owing to the long-range character of the Coulomb interaction, the large-scale fluctuations of the impurities (having a dimension larger than the average distance) can lead to an appreciable scatter of the levels. At  $K \ll 1$  this potential adds to formula (4.41) a correction of the order of<sup>[76]</sup>  $K^{1/4}$ . At  $1 - K \ll 1$  the contribution of the large-scale fluctuations can change the numerical coefficient in (4.42) if the impurities are randomly disposed. On the other hand, if a correlation exists in the disposition of the impurities, there may be no large-scale fluctuations then at  $1 - K \ll 1$ , and the activation energy is determined by formula (4.42). Such a correlation is the result of the interaction of the impurities in the melt and

is fixed because the diffusion of the impurities changes abruptly during the crystallization process.<sup>[77]</sup> There is no correlation, for example, when the impurity centers are produced by radiation at temperatures so low that these centers are immobile, or in the case of a narrow-band semiconductor, when the correlation is weakened by the intrinsic carriers that are present during the solidification of the sample.<sup>[78]</sup>

An investigation of the properties of the large-scale potential is reported in<sup>[11,76]</sup>. This question is outside the scope of the present review. We have reported only the results of the cited papers and focused attention only on how to determine the activation energy from a given distribution of the potential.

At  $K \ll 1$ , the large-scale potential  $V(r)$  is Gaussian. Its distribution function  $F(V)$  and the characteristic scale  $r_0$  are determined by the relations

$$F(V) = \frac{e}{\gamma \sqrt{\pi}} e^{-(eV)^2/\gamma^2}, \quad \gamma = 0.26 e_D K^{1/4}, \quad (4.43)$$

$$r_0 \approx N_D^{-1/3} K^{-1/2}. \quad (4.44)$$

In the case of strong compensation,  $1 - K \ll 1$ , the potential is not Gaussian. It contains all the spatial harmonics of scale smaller than  $r_0$ . The maximum scale  $r_0$  is determined by the electron screening, which turns out in this case to be nonlinear. The amplitude of the potential increases with scale, so that the maximum swing of the potential  $\gamma$  is possessed by the fluctuations with dimension  $r_0$ . According to<sup>[11]</sup>,

$$\gamma \approx \frac{e^2 N_D^{1/3}}{\kappa (1-K)^{1/3}}, \quad r_0 \approx N_D^{-1/3} (1-K)^{-2/3}. \quad (4.45)$$

Taking into account the large-scale potential, the energy of the overwhelming majority of levels is equal not to zero, as was assumed in the derivation of (4.40), but to  $eV(r)$ . This quantity changes little over distances that are small in comparison with  $r_0$ . Inasmuch as both at  $K \ll 1$  and at  $1 - K \ll 1$  we have  $r_0 \gg N_D^{-1/3}$  for transitions between neighboring impurities, we can neglect the difference  $\epsilon_i - \epsilon_j$  in (4.12). Then the quantity

$$\epsilon_{ij} = |\mu - eV(r)| \quad (4.46)$$

does not depend on  $r_{ij}$ .

Let us see now how the large-scale potential alters the result (4.40) at  $K \ll 1$  and  $1 - K \ll 1$ . In accordance with (4.29) we should average (4.46) with the distribution function of the large-scale potential  $F(V)$ . If  $K \ll 1$  then, owing to the symmetry of  $F(V)$  with respect to zero, the result agrees with (4.41) with exponential accuracy. At  $1 - K \ll 1$  the explicit form of the distribution function is not known. All we know is that  $F(V) \equiv 0$  at<sup>[11]</sup>  $eV(r) < \mu$ . Therefore averaging of (4.46) yields

$$\epsilon_s = |\mu - e\langle V(r) \rangle| = C_1 \frac{e_D}{(1-K)^{1/3}}, \quad (4.47)$$

where  $C_1$  is an unknown constant on the order of unity.

As  $K \rightarrow 0$  and  $K \rightarrow 1$ , the correlation length  $r_0$  of the potential increases without limits in accordance with (4.44) and (4.45). From the statements made in Sec. (e) it follows that formula (4.29) no longer holds at a certain critical value of  $r_0$ . Without stopping now to find this critical value, we proceed to describe the macroscopic approach which makes it possible to calculate the activation energy at still larger values of  $r_0$ . We consider a volume whose linear dimensions are

small in comparison with  $r_0$ , so that all the  $\epsilon_{ij}$  inside the volume can be regarded as the same. On the other hand, let this volume be sufficiently large in the sense that the dispersion of the percolation threshold  $\xi_c$ , due to the fact that the threshold is finite, is small in comparison with the characteristic values of  $\gamma/T$ . It is then possible to introduce the concept of local conductivity, which depends on the coordinates like  $\exp[-\epsilon_3(r)/T]$ , where in analogy with (4.40) we have  $\epsilon_3(r) = |\mu - eV(r)|$ . To calculate the effective electric conductivity of a semiconductor we can now use the percolation method in its continual formulation (Chap. 3).

In the case of strong compensation we have  $eV(r) \ll \mu$  in practically all of space. Therefore the low-resistance regions are those with small values of  $eV(r)$  and the activation energy  $\epsilon_3 = eV_c - \mu$ , where  $V_c$  is in accordance with the terminology of Chap. 2, is the percolation level of the potential  $V(r)$ . Then

$$\epsilon_3 = C_2 \frac{eD}{(1-K)^{1/3}} \quad (4.48)$$

where  $C_2$  is a numerical coefficient, as yet unknown, smaller than  $C_1$ .

For weak compensation, to the contrary,  $eV(r) \ll \mu$ . Therefore the activation energy is equal to the difference  $\mu - eV'_c$ , where  $V'_c$  is the upper percolation level in the potential  $V(r)$ . As already mentioned, at  $K \ll 1$  the potential  $V(r)$  is Gaussian. In a Gaussian potential, according to<sup>[33]</sup>, the critical fraction of the space which corresponds to the onset of percolation is equal to 0.17. Therefore the upper percolation level is equal to  $0.67\gamma/e$ , where  $\gamma$  is given by (4.43). Thus,

$$\epsilon_3 = 0.61eD(1 - 0.29K^{1/4}). \quad (4.49)$$

We now discuss the regions of applicability of the macroscopic approach to perturbation theory.

According to the results of Chap. 5, the volume in which the dispersion  $\xi_c$  is small should have in comparison with  $\gamma/T$  parameters larger than the length

$$L = a\xi_c \left( \frac{\gamma}{T\xi_c} \right)^{-\nu}, \quad (4.50)$$

which is the correlation radius (5.25) of an infinite cluster at  $\xi - \xi_c = \gamma/T$ . Thus, the macroscopic approach is applicable if  $L \ll r_0$ . On the other hand, it should be clear from Chap. 5 that  $L$  is indeed the characteristic distance between the elements essential for the percolation. Therefore the result of perturbation theory (4.29) is valid at  $L \gg r_0$ .

A comparison of the formulas for  $\epsilon_3$  with experiment is discussed in the review<sup>[17]</sup>. The agreement of formulas (4.41) and (4.49) with numerous experimental data for the case of a lower degree of compensation can be regarded as good. The situation is more complicated in the case of strong compensation when, on the one hand, the theory does not make it possible to determine the numerical factors  $C_1$  and  $C_2$ , and on the other hand, by virtue of the technological inhomogeneities in the samples, the degree of compensation can vary strongly from point to point. At the present time it can be regarded as established only that  $\epsilon_3$  increases rapidly as  $K \rightarrow 1$  in accordance with a law that is close to  $(1 - K)^{-1/3}$ .<sup>[79]</sup>

So far we have said nothing concerning the intermediate compensation  $K \approx 0.5$ . The calculation of  $\epsilon_3$  en-

counters in this case difficulties of twofold character. First, in the case of intermediate compensation, the many-electron problem of the distribution of the electrons over the impurities at  $T = 0$  does not have small parameters and has not been solved completely to this day<sup>2)</sup> (although the density of states in the immediate vicinity of the Fermi level has been obtained<sup>[72]</sup>). This difficulty can be overcome in principle by solving the problem with a computer and then using the prescription (4.29).

The second difficulty has a more fundamental character. It consists in the fact that in the derivation of the statement concerning the equivalent resistance network we neglect the correlations of the distribution functions at the neighboring sites (see<sup>[12]</sup>), and take the electron interaction into account only in the self-consistent-field approximation. This description seems to us perfectly correct in the limiting cases of small and large compensation. The reason is that in both cases the number of carriers (vacancies at  $K \ll 1$  and electrons at  $1 - K \ll 1$ ) in the region of the peak of the density of states is small and the probability that they will turn out to be at neighboring sites is negligible. As to the self-consistent potential, it turns out to be large-scale in both cases, i.e., it is produced by a large number of electrons and fluctuates little.

These considerations, however, are no longer valid in the case of intermediate compensation, when the electron goes over frequently from levels lying above the Fermi level to levels below it, and the potential at the donor is produced by its nearest neighbors. In this case it remains unclear whether it is possible to use a random network of resistors as a model to describe the temperature dependence of hopping conductivity. (The results of Sec. (c), naturally, are not sensitive to neglect of the correlation effects and are valid for all  $K$ .)

## 5. SINGULARITIES NEAR THE PERCOLATION THRESHOLD AND ASSOCIATED PHYSICAL PROBLEMS

### a) Critical Exponents

In the preceding chapters we have discussed principally one aspect of percolation theory, the determination of the threshold corresponding to the onset of an infinite cluster. We have shown that the threshold values suffice to solve a whole number of physical problems. In this chapter we proceed to other problems, which are also formulated in terms of percolation theory, but call for the study of the critical behavior near the percolation threshold.

In percolation theory it is possible to introduce certain quantities that have singularities near the threshold. In analogy with the theory of second-order phase transitions, it is customarily assumed that these singularities have a power-law behavior. One such quantity is the previously introduced density  $P(x)$  of the infinite cluster, which is analogous to the ordering parameter

<sup>2)</sup>Exceptions are semiconducting solid solutions, where the principal cause of the scatter of the impurity levels may be fluctuations of the composition. In this case one can disregard the interaction of the electrons with one another, and the distribution of the impurity levels can be easily obtained. <sup>[80]</sup>

of the theory of phase transitions. Its behavior near the percolation threshold is investigated by computer calculations. For the node problem on three different three-dimensional lattices, the Monte Carlo method yields at  $x - x_c \ll x_c$

$$P(x) \sim (x - x_c)^\beta, \quad (5.1)$$

where  $0.3 \leq \beta \leq 0.4$ .<sup>[36]</sup> For the node problem on a planar triangular lattice, a value  $\beta = 0.14 \pm 0.03$  was obtained by using series.<sup>[81]</sup> The agreement between the values of  $\beta$  for different lattices with the same number of dimensions suggests that  $\beta$ , together with other exponents to be determined below, depends only on the dimensionality of the space and does not depend on the rules that determine the bonds at short distances.<sup>[15]</sup> It is reasonable, in particular, to assume that the same exponent  $\beta$  describes the increasing fraction of sites belonging to an infinite cluster with increasing  $r - r_c$  or  $B - B_c$  in random-node problems, and the increase in the volume of the connective black space with increasing  $V - V_c$  in the continual problem. This assumption is in the spirit of modern theory of phase transitions, in which it is assumed that the character of the interactions at short distances has little effect on the critical exponents. To be sure, in the theory of phase transitions, even for one dimension of space there remains a weak dependence of the exponents on a number of components of the order parameter, and this dependence leads, for example, to the difference between the Ising and the Heisenberg models. In all the problem classes considered above, the local characteristics are single-component (broken or unbroken bond, black or white color, etc.). One could therefore assume that in the percolation problems the exponents should be universal. As will be shown below, none of the available data contradict this hypothesis.

We now introduce the quantity  $n_s$ , which is the average number of clusters of  $s$  sites per lattice site. For the sake of argument we consider the site problem, although the statements made below can be easily extended to any other problem of percolation theory. It is assumed that the given site belongs to a cluster of  $s$  sites, that it wets  $s - 1$  other sites. The quantity  $m_1 = \sum_s s n_s$  is the fraction of the sites belonging to the finite clusters. Subtracting it from the fraction of all the open sites  $x$ , we obtain the previously introduced fraction of sites belonging to the infinite cluster

$$P(x) = x - m_1(x). \quad (5.2)$$

Another quantity having a singularity at the point  $x_c$  is the so-called "average cluster dimension"<sup>[23]</sup>

$$S(x) = \sum_s n_s s^2. \quad (5.3)$$

We note that the cluster dimension is averaged in (5.3) not over the clusters but over all the sites. It has been established<sup>[24]</sup> that for all the investigated lattices we have at  $x \rightarrow x_c - 0$

$$S(x) \sim (x_c - x)^{-\gamma}, \quad (5.4)$$

with

$$\gamma = \begin{cases} 2.38 \pm 0.03 & \text{if } d=2, \\ 1.69 \pm 0.05 & \text{if } d=3, \end{cases} \quad (5.5)$$

where  $d$  is the number of dimensions.

An important step in percolation theory was the work of Kasteleyn and Fortuin<sup>[20]</sup>, who showed that the functions  $P(x)$  and  $S(x)$  introduced above and the function

$F(x) = \sum_s n_s$  are connected with one another as thermodynamic functions that enter in the theory of critical phenomena. If we use the terminology of a ferromagnetic system, then the function  $F(x)$  is equivalent to the free energy,  $P(x)$  is equivalent to the spontaneous magnetization, and  $S(x)$  is equivalent to the magnetic susceptibility. The quantity  $x$  is equivalent to the temperature  $T$ , the region  $x < x_c$  corresponding to the paramagnetic region  $T > T_c$  while  $x > x_c$  corresponds to the ferromagnetic region. To prove this, we introduce, following<sup>[20,82]</sup>, a parameter  $h$  which plays the role of the dimensionless magnetic field  $\mu H/T$ , where  $\mu$  is the spin magnetic moment. We imagine an additional site (the "demon" of Kasteleyn and Fortuin), which does not belong to the considered lattice but is bound by definition to each of its sites with a probability  $1 - e^{-h}$ . It is clear that in the presence of this demon an infinite cluster of open sites exists at arbitrarily small values of  $x$ . As  $x \rightarrow 0$  we have  $P(x, h) \rightarrow xh$ . At finite  $h$  the total number of finite clusters per lattice site can be represented in the form

$$F(x, h) = \sum_s n_s e^{-hs}. \quad (5.6)$$

The factor  $e^{-hs}$  is the fraction of the clusters with dimension  $s$  in which not a single site is bound to the demon. This quantity is indeed analogous to the free energy. We consider its derivatives with respect to  $h$

$$m_j(x) = (-1)^j \frac{\partial^j}{\partial h^j} F(x, h) |_{h=0} = \sum_s s^j n_s. \quad (5.7)$$

The function  $m_1$  is connected with  $P(x)$  by formula (5.2), while  $m_2 \equiv S(x)$  and is analogous to the susceptibility. Therefore the symbols used in (5.1) and (5.4) are traditional for the exponents of critical phenomena. Differentiating  $F(x, h)$  with respect to both arguments, we can obtain a set of functions that are analogous to all the remaining thermodynamic quantities investigated in the theory of critical phenomena.

Continuing the analogy with the theory of phase transitions, we introduce the concept of the correlation radius<sup>[70,83]</sup> in percolation problems. To this end we define for the lattice sites a quantity  $g(r, r')$  equal to unity if the sites with the coordinates  $r$  and  $r'$  wet each other and do not belong to an infinite cluster, and equal to zero in all other cases. We then introduce the correlation function  $G(r - r')$  by averaging  $g(r, r')$  over all the lattice sites

$$G(|r - r'|, x) = \langle g(r, r') \rangle. \quad (5.8)$$

It is obvious that  $G(r, x) \rightarrow 0$  as  $r \rightarrow \infty$ . We shall assume that it contains a single characteristic length, which we shall call the correlation radius  $L$ . Just as in the theory of phase transitions,  $L \rightarrow \infty$  as  $x \rightarrow x_c$  and behaves in the following manner:

$$L \sim \frac{1}{|x - x_c|^\nu}. \quad (5.9)$$

In percolation theory this has a simple meaning, inasmuch as it characterizes the increase of the average diameter of the clusters when the percolation threshold is approached. At  $x > x_c$  the correlation radius describes also the characteristic dimension of the network which is formed by the infinite cluster. From the definitions (5.3) and (5.8) follows the important relation

$$S(x) = \sum_r G(r, x), \quad (5.10)$$

which is perfectly analogous to the well known relation for the susceptibility.

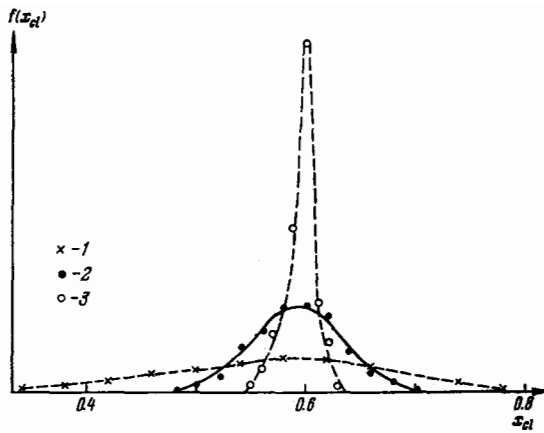


FIG. 6. Distribution functions of the quantities  $x_{cl}$ . 1)  $l = 8$ , 2)  $l = 32$ , 3)  $l = 128$ .

A convenient method for finding the correlation radius appears in the study of percolation in finite volumes. We consider the problem of percolation from phase to phase in a finite cube with side  $l$ . We increase the fraction of open sites, gradually adding new randomly-located open sites to those already existing. At a certain value  $x = x_{cl}$ , percolation from phase to phase occurs. In view of the finite volume,  $x_{cl}$  is not duplicated when the experiment is repeated. One can speak only of a distribution function  $f(x_{cl})$  of the quantity  $x_{cl}$ . As  $l \rightarrow \infty$  we have  $f(x_{cl}) \rightarrow \delta(x_{cl} - x_c)$ . Figure 6 shows the functions  $f(x_{cl})$  calculated with a computer for a quadratic lattice.<sup>[83]</sup> We see that the shift of the average value  $\langle x_{cl} \rangle$  relative to  $x_c$  is small in comparison with the width of the curve. A similar situation occurs also in the three-dimensional case.<sup>[54]</sup> We introduce the quantity  $W_l = \sqrt{\langle (x_{cl} - \langle x_{cl} \rangle)^2 \rangle}$  and assume that it decreases with increasing  $l$  in power-law fashion

$$W_l = \frac{B}{l^{1/\nu}}. \quad (5.11)$$

This quantity was investigated in<sup>[54, 55, 83, 84]</sup>. In<sup>[54]</sup> there was obtained for the random-site problem at  $d = 3$

$$\nu = 0.83 \pm 0.13 \quad (5.12a)$$

(the error is estimated by us in accordance with the figure given in<sup>[54]</sup>). In<sup>[83]</sup>, for the site problem on cubic and quadratic lattices, we obtained

$$\nu = \begin{cases} 0.90 \pm 0.05 & \text{if } d = 3, \\ 1.33 \pm 0.05 & \text{if } d = 2. \end{cases} \quad (5.12b)$$

In<sup>[84]</sup> the value obtained for a primitive cubic, body-centered cubic, and planar triangular lattices were  $\nu = 0.97 \pm 0.04$ ,  $\nu = 0.92 \pm 0.04$ , and  $\nu = 1.36 \pm 0.04$ , respectively. It can be shown that the exponent  $\nu$  in (5.11) coincides with the exponent of the correlation radius in (5.9).<sup>[70]</sup> We introduce the probability  $Q_l(x)$  that percolation over a cube of dimension  $l$  is possible:

$$Q_l(x) = \int_0^x f(x') dx'. \quad (5.13)$$

This quantity is a function of the argument

$$\frac{x - x_c}{W_l} = \text{sign}(x - x_c) \left( \frac{l}{L} \right)^{1/\nu}, \quad \text{where } L = \frac{B\nu}{|x - x_c|^\nu}. \quad (5.14)$$

If  $x - x_c < 0$ , then at  $l \leq L$  the probability  $Q_l(x)$  depends little on  $l$ , and as  $l \rightarrow \infty$  the probability  $Q_l(x) \rightarrow 0$ . At  $x > x_c$ , the same properties are possessed by the quantity  $1 - Q_l(x)$ . Thus, the quantity  $L$  defined in (5.14) characterizes the dimensions of the clusters and is the correlation radius. The exponent of the correla-

tion radius is determined by (5.12) and is the third known exponent of percolation theory.

The natural way to establish the connection between the exponents introduced above is to formulate a similarity hypothesis.<sup>[82, 83]</sup> By analogy with the theory of phase transitions<sup>[85]</sup>, we assume that the singular parts of the functions satisfy the relations

$$F(\tau^y, h^z) = l^d F(\tau, h), \quad (5.15)$$

$$G(r, \tau) = l^{-d+2-\eta} G(r l^{-1}, \tau l^y), \quad (5.16)$$

where  $\tau = (x - x_c)/x_c$ , and  $y$ ,  $z$ , and  $\eta$  are as-yet unknown exponents. With the aid of (5.15) and (5.16), and also (5.2), (5.7), and (5.10), all the percolation-theory exponents introduced so far can be expressed in terms of two of them, for example, in terms of  $y$  and  $z$ . We shall not write out all the relations between these exponents, which are perfectly analogous to the relations that follow from the statistical similarity hypothesis in the theory of phase transitions.<sup>[85]</sup> We shall dwell only on the relation between the three exponents investigated in percolation theory:

$$\nu = \frac{\gamma + 2\beta}{d}. \quad (5.17)$$

According to (5.1) and (5.5) the right-hand side of (5.17) is equal  $1.33 \pm 0.05$  at  $d = 2$  and  $0.80 \pm 0.05$  at  $d = 3$ ; the good agreement with the calculated values at  $d = 2$  and the somewhat worse agreement at  $d = 3$  is clearly seen.

The exponent  $\eta$  can be calculated with aid of the relation

$$\eta = 2 - \frac{\gamma d}{2\beta + \gamma}. \quad (5.18)$$

$\eta = 0.22 \pm 0.05$  at  $d = 2$  and,  $\eta = -0.09 \pm 0.012$  at  $d = 3$ .

In addition to the three exponents  $\beta$ ,  $\gamma$ , and  $\nu$  considered above, one more exponent, which apparently has no analog in the theory of phase transitions, was investigated. It is connected with the behavior at  $x > x_c$  of the conductivity  $\sigma(x)$  produced if identical finite resistance values are assigned to all unbroken bonds and zero values to all the broken bonds. Then

$$\sigma(x) \sim (x - x_c)^t. \quad (5.19)$$

The quantity  $\sigma(x)$  is meaningful not only for the bond problem, but also for the site problem. In this case, when determining the lattice conductivity, it is necessary to assume that all the bonds are made up of identical resistors, and in each closed site the connection between all the resistances that emerge from it is broken. Moreover, a similar quantity can be easily introduced also in continual problems. If it is assumed that the regions where  $V(\mathbf{r}) < V$  have identical electric conductivity  $\sigma_0$ , and the regions with  $V(\mathbf{r}) > V$  are filled with insulator, then at  $V \rightarrow V_c + 0$  we have

$$\sigma(V) \sim (V - V_c)^t.$$

The first investigation of  $\sigma$  was made by Last and Thouless<sup>[86]</sup>. They punched round holes with centers located at the sites of a square lattice, in a square sheet of conducting graphite paper and the resistance between opposite sides of the square was measured as a function of the number of holes (the holes corresponding to the nearest sites were covered). Owing to the large statistical scatter of the data given in<sup>[86]</sup>, it was possible to establish only the inequality  $1 < t < 2$ . More detailed investigations were carried out for lattice problems. The site problem was investigated with the aid of a cube

assembled of  $16 \times 16 \times 16$  standard resistors<sup>[87]</sup> or with the aid of a piece of a standard metallic screen with  $137 \times 137$  cells.<sup>[88]</sup> In both cases, the contacts at the lattice sites were broken in accordance with data from a random-number generator. Simultaneously with decreasing fraction of intact sites, measurements were made of the resistance between the opposite faces of the cube and opposite sides of the square. As a result, the exponent values obtained for the site problem were  $t_3 = 2$  and  $t_2 = 1.38$  for two and three dimensions, respectively. In addition to direct simulation of lattice problems, the electric conductivity was calculated by computer solution of the system of Kirchhoff's equations.<sup>[36,87]</sup> Calculation<sup>[87]</sup> has confirmed the result  $t_3 = 2$  of the model experiment. On the other hand, Kirkpatrick<sup>[36]</sup>, in a calculation of the resistance of cubes with as many as  $25 \times 25 \times 25$  cells, obtained for the bond problem  $t_3 = 1.6 \pm 0.1$  and for the site problem  $t_3 = 1.5 \pm 0.2$ . The reason for the discrepancy between these quantities and the result of<sup>[87]</sup> is still not clear. For two dimensions, Kirkpatrick<sup>[36]</sup> obtained  $1 < t_2 < 1.3$ , which also differs somewhat from the experimental value of<sup>[86]</sup>.

It is reasonable to assume that the exponent  $t$  can yield important additional information on the topology of the infinite cluster. However, the problem of extracting this information by an analysis of the values of  $t$ ,  $\beta$ ,  $\gamma$ , and  $\nu$  has not yet been solved. We shall therefore dwell only briefly on three steps in this direction.

Last and Thouless<sup>[86]</sup> reasoned in the following manner: Assume that at any  $x$ , roughly speaking,  $1/3$  of the sites belonging to the IC makes up chains that join any two opposite faces of the cube. Then the number of chains, and consequently also  $\sigma(x)$ , should be proportional to  $P(x)$ , i.e., the exponent  $t$  should coincide with  $\beta$ . In fact, however,  $\beta < t$ , i.e., near the threshold  $\sigma(x)$  increases with increasing  $x$  much more slowly than  $P(x)$ . This means that actually the overwhelming part of the IC does not play any role in the electric conductivity. According to Last and Thouless, this part is concentrated in chains that are truncated (have dead ends). This conclusion, however, cannot be regarded as unambiguous. The ineffectiveness of the IC from the point of view of the electric conductivity might be connected with the large number of the long chains which duplicate small sections of short chains.

The authors of<sup>[89]</sup> have proposed that if one discards the dead ends, then the remaining part of the IC is a random network with characteristic distance between nodes equal to the correlation radius  $L$ , and the chains joining the nodes of this network (the macrobonds) are not duplicated (are single-path) at least over half of their length. It follows from this assumption<sup>[89]</sup> that the length of the macrobond  $\mathcal{L}$  is of the order of  $(x - x_c)^{-1}$ , and that  $t = 1 + \nu = 1.9$  to  $2$  at  $d = 3$  and  $t = 1$  at  $d = 2$ . These values of  $t$ , especially for  $d = 3$ , are not too far from the results of the calculations and measurements. This reasoning<sup>[89]</sup>, however, is meaningful only when the length of the macrobond  $\mathcal{L}$  is not shorter than the distance  $L$  between its ends, i.e., at  $\nu \leq 1$ . As we have seen above, it was found recently that  $\nu = 1.3$  at  $d = 2$ . Consequently, in the two-dimensional case the model of a single-conductor network is not applicable. The problem of the adequacy of this model in the three-dimensional case, where  $\nu \approx 0.9$  to  $1$ , remains open. A refinement of the experimental and calculated values of the exponent  $t$  would make the situation clearer.

Finally, one more approach to this problem, proposed in<sup>[90]</sup>, makes it possible to connect the exponent  $t$  with the correlation-radius exponent  $\nu$  without resorting to concrete models. This approach is based on the similarity hypothesis. The network of resistors is strongly inhomogeneous in all scales that are smaller than the correlation radius. In accordance with the similarity hypothesis, we assume that the large-scale structure of this network remains similar to itself with changing  $\tau = |x - x_c|$ , and increases with a scale factor  $\tau^{-\nu}$ . Of course, this does not pertain to the small-scale structure which contains a minimal length equal to the lattice constant. Further, one more important assumption is needed, namely that the resistance of the network be determined by the large-scale structure. Then the resistance  $R$  of a cube having a linear dimension on the order of the correlation radius  $L$  varies with in accordance with  $R \sim L \sim \tau^{-\nu}$ . On the other hand, a cube with dimension  $L$  can be treated macroscopically, and therefore the specific conductivity of the system is connected with  $R$  by the usual relation

$$\sigma = \frac{L^{d-2}}{R} \sim \tau^{v(d-1)}.$$

Thus,

$$t = \begin{cases} 2\nu, & d = 3, \\ \nu, & d = 2. \end{cases} \quad (5.20)$$

According to (5.12), (5.17), (5.1), and (5.5) the exponent is  $\nu = 1.33 \pm 0.05$  at  $d = 2$ , in good agreement with the results of<sup>[36,88]</sup>. In the three-dimensional case the agreement is also satisfactory.

We note, however, that the assumptions made in the derivation of (5.20) reject the possibility of the macrobonds of the network being strongly twisted (having a coiled structure). By examining the breaking of the IC with decreasing  $x$ ,<sup>[89]</sup> one can present arguments favoring the assumption that the absence of a coiled structure at an arbitrary duplication of the macrobonds is equivalent to the condition  $\nu \geq 1$ . This condition is satisfied at  $d = 2$ . In the three-dimensional case  $\nu$  is close to unity so that the situation is not clear enough.

We proceed now to discuss physical problems in which the electric conductivity is expressed in terms of the critical exponents of percolation theory. In those cases when there are grounds for assuming that the system is a mixture of elements of only two types—conducting and nonconducting—the determination of electric conductivity reduces to a calculation of  $\sigma(x)$ .<sup>[36]</sup> It is assumed that these problems include the question of the electric conductivity of tungsten bronzes  $M_xWO_3$  with changing concentration  $x$  of the alkali metal. According to<sup>[7]</sup>, experiments yield a relation of the type (5.19) with  $t = 1.8 \pm 0.2$  and  $x_c = 0.17$ . The dependence of the electric conductivity of mercury on its density near the critical point and the dependence of the electric conductivity of metal-ammonia solutions with changing metal concentration have a similar form.<sup>[8]</sup> It is interesting to note that in all these cases the point  $x_c$  is singular also for the Hall constant:  $R_H(x) \sim (x - x_c)^{-g}$ , where  $0 < g < 1$ . Kirkpatrick<sup>[8]</sup> advanced arguments favoring the assumption that  $R_H(x) \approx p^{-1}(x)$  as  $x \rightarrow x_c$ , i.e.,  $g = \beta$ . These arguments are criticized in<sup>[89]</sup>, where it is stated on the basis of the model of a single-path network that  $g = \nu$  at  $d = 3$ . Considerations similar to those proposed in<sup>[89]</sup> lead to the conclusion that  $g = 0$  in the two-dimensional case. By a more

general method, using the arguments that have led to (5.20), it is possible to obtain the same results.<sup>[90]</sup> In<sup>[90]</sup> they measured the Hall constant of conducting paper with randomly punched holes. It turned out that as the percolation threshold is approached  $R_H$  does not depend on the number of holes. This agrees with the results described above.

We now turn to applications connected with hopping conductivity.

### b) Electric Conductivity of Semiconducting Films

Amorphous semiconductors in which hopping conductivity is investigated are obtained as a rule in the form of films. Even in sufficiently thick films there is observed a very strong dependence of the resistivity on the film thickness  $b$ .<sup>[91,92]</sup> To calculate the exponent of the electric conductivity along the film  $\sigma_f$ , we use the general prescription (4.13), i.e.,

$$\sigma_f(b) = \sigma_0 e^{-\xi_{cb}}, \quad (5.21)$$

where  $\xi_{cb}$  is the threshold value of  $\xi$ , at which there appears for the first time an IC of sites situated inside the film and bound to one another in accordance with the criterion (4.14). If we imagine all of space to be filled with sites having the same concentration as in the interior of the film, then it is obvious that the film IC is always part of a three-dimensional IC, and exists only when the three-dimensional one exists. If, however,  $\xi$  is very close to the three-dimensional  $\xi_c$ , then the three-dimensional IC can become so rare that it breaks up inside the film into individual unconnected pieces, and there exists no film IC. It is therefore clear that  $\xi_{cb} > \xi_c$ . It is obvious that  $\xi_{cb}$  depends on the parameter  $b/a\xi_c$ , where according to (4.14)  $a\xi_c$  is of the order of the average distance between the nearest bound site (the average length of the hop). According to (4.16) and (4.36)

$$a\xi_c \approx N^{-1/3} \quad (5.22)$$

is the regime of conductivity with constant activation energy, and

$$a\xi_c \approx a \left( \frac{T_0}{T} \right)^{1/4} \quad (5.23)$$

in the regime of Mott conductivity.

At  $ba\xi_c \ll 1$  we have simply the two-dimensional percolation problem ( $\xi_{cb} \equiv \xi_{c2}$ ). Under conditions of Mott hopping conductivity, by analogy with the derivation of (4.36), we can obtain<sup>[71,93-95]</sup>

$$\xi_{cb} = \left( \frac{T_{02}}{T} \right)^{1/3}, \quad (5.24)$$

where  $T_{02} = \tilde{\lambda} (g(\mu) a^2 b)^{-1}$ , and  $\tilde{\lambda} = 13.8 \pm 0.8$ .<sup>[74]</sup> Formula (5.24) was experimentally confirmed in<sup>[94]</sup>. The determination of the parameters  $T_0$  and  $T_{02}$  which enter in expressions (4.2) and (5.24), has made it possible to obtain  $g(\mu)$  and  $a$  in amorphous Ge.<sup>[94]</sup>

In<sup>[96]</sup> they obtained the function  $\xi_{cb}$  at  $b/a\xi_c \gg 1$ , using heuristic considerations based on a representation of the three-dimensional IC as a certain network with characteristic dimension equal to the correlation radius  $L(\xi)$ , which takes for the random-site problem the form

$$L(\xi) \approx a\xi_0 \left( \frac{\xi_c}{\xi - \xi_0} \right)^\nu \quad \text{and} \quad \frac{\xi - \xi_0}{\xi_0} \ll 1. \quad (5.25)$$

Within the framework of this representation it is obvious

that if  $L(\xi) \gg b$  then parts of the three-dimensional IC are not joined into a film IC. At the same time, at  $L(\xi) \ll b$  there are many layers of the network of the three-dimensional IC, forming a film IC, in the interior of the film. Thus,  $\xi_{cb}$  is determined by the condition  $L(\xi_{cb}) = b$  or

$$\xi_{cb} = \xi_0 \left[ 1 + D \left( \frac{a\xi_0}{b} \right)^{1/\nu} \right], \quad (5.26)$$

where  $D$  is an unknown number of the order of unity and  $\nu$  is the exponent of the correlation radius of the three-dimensional problem.

The question of the dependence of the threshold of percolation along a bulk bounded by two parallel planes can be regarded also with the site problem as an example. If the boundary planes are spaced  $n$  lattice periods apart, then reasoning analogous to that given above yields

$$x_c(n) = x_c(\infty) \left( 1 + \frac{D_1}{n^{1/\nu}} \right). \quad (5.27)$$

In<sup>[94]</sup>, an attempt was made to verify formula (5.27) by direct calculation of  $x_c$  of the site problem on a simple cubic lattice by the Monte Carlo method, with  $n$  running through the values from 1 to 10. It turned out that the function  $x_c(n)$  agrees well with the (5.27) with  $\nu = 1 \pm 0.08$ , which agrees with in the limits of errors with the results given above for the exponent of the correlation radius at  $d = 3$ .

Formula (5.27) is analogous to the expression for the transition temperature of a ferromagnetic film consisting of  $n$  atomic layers

$$T_{cn} = T_{c\infty} \left( 1 + \frac{D_2}{n^{1/\nu}} \right),$$

where  $\nu$  is the three-dimensional correlation-radius exponent of the magnetic moment. This formula was quite convincingly confirmed by numerical calculations.<sup>[97,98]</sup>

It is seen from (5.26) and (5.21) that the resistance begins to increase exponentially with decreasing  $b$  at  $b \approx (a\xi_c)\xi_c^\nu$ , i.e., still at  $b/a\xi_c \gg 1$ . Under conditions of hopping conductivity it follows from (5.26) and (5.21) that

$$\ln \frac{\sigma_f(b)}{\sigma(\infty)} = -D \left( \frac{T_0}{T} \right)^{\frac{\nu+1}{4\nu}} \left( \frac{a}{b} \right)^{1/\nu}, \quad (5.28)$$

where according to (5.12),  $\nu \approx 0.9$ .

### c) Pre-exponential Factor of the Hopping Conductivity

We have discussed so far only the structure of the exponential factor of the hopping conductivity. It should be clear from Chap. 3, to obtain the pre-exponential factor  $\sigma_0$  in formula (4.13) we need information on the topology of the IC near the percolation threshold. This question was discussed in<sup>[38,99]</sup> on the basis of concrete assumptions concerning the structure of IC. In<sup>[54,99]</sup> a general derivation was given of a formula for hopping conductivity, which made it possible to determine the pre-exponential factor and which was based only the concept of percolation in a finite volume. We shall present this derivation below.

Let us find the electric conductivity of a random network with resistors (4.9). To this end we consider a cube with a side  $l$  so small that at a given scatter of the resistances  $R_{ij}$  it is possible to assume, with good accuracy, that all the resistances of the cube are deter-



mined by the resistance of one element. This element has the largest resistance of all the other elements that must be included (starting with the smallest) in order for percolation from face to face to occur. Let the corresponding  $\xi_{ij}$  be equal to  $\xi_{c,l}$ . Then the specific electric conductivity  $\sigma_l$  of the considered cube is equal to

$$\sigma_l = (R_0 l)^{-1} e^{-\xi_{c,l}}. \quad (5.29)$$

In accordance with the statements made in Sec. (a),  $\xi_{c,l}$  fluctuates from realization to realization, and its mean-square fluctuation is described by the formula

$$W_l = B' \xi_{c,l} \left( \frac{a \xi_{c,l}}{l} \right)^{1/\nu}, \quad (5.30)$$

where  $a \xi_{c,l}$  is of the order of the average distance between the nearest bound sites, determined by (5.22) and (5.23). With increasing  $l$ , the maximum resistance ceases to play a special role and  $\sigma_l$  no longer depends on  $l$ , since the number of the essential resistors becomes proportional to the volume of the cube. Then  $\sigma_l$  coincides with the sought specific conductivity of the macroscopic system. Another criterion of the transition from the condition (5.29) to the macroscopic electric conductivity with increasing  $l$  is the vanishing of the large relative fluctuations of  $\sigma_l$ . This occurs at  $W_l \approx 1$ , i.e.,

$$l = L \approx (a \xi_{c,l})^{\nu}. \quad (5.31)$$

Substituting (5.31) in (5.29) we obtain ultimately

$$\sigma \approx (R_0 a)^{-1} \xi_{c,l}^{-1-\nu} e^{-\xi_{c,l}}. \quad (5.32)$$

According to (5.31) and (5.25) the characteristic dimension of the network which determines the electric conductivity of the system is of the order of the correlation radius at  $\xi - \xi_c \approx 1$ . This seems natural in view of the exponential dependence of  $\sigma_l$  on  $\xi_c$ . According to (4.16) and (4.36) we have

$$\sigma \approx (R_0 a)^{-1} (N^{1/3} a)^{1+\nu} e^{-(2r_c/a) + (e_s/T)} \quad (5.33)$$

in the regime of constant activation energy and

$$\sigma \approx (R_0 a)^{-1} \left( \frac{T_0}{T} \right)^{-(1+\nu)/4} \exp \left[ - \left( \frac{T_0}{T} \right)^{1/4} \right] \quad (5.34)$$

in the regime of Mott conductivity. We note that the presented derivation does not make it possible to determine the numerical coefficient of the pre-exponential factor in formulas (5.32)–(5.34). In addition, it must be kept in mind that we have considered a model in which the resistance of the elements is defined by (4.9), with  $R_0$  independent of the indices  $i$  and  $j$  of the sites. If  $R_0$  depends on  $\xi_{ij}$ , then the generalization of the result consists of substituting in (5.32) the quantity  $R_0 | \xi_{ij} = \xi_c$ , which can introduce an additional power-law dependence on  $N$  and  $T$ .<sup>[36, 39]</sup>

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