Impurity conduction near the metal-insulator transition point

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The low-temperature conductivity of doped semiconductors near the metal-insulator transition point is described by a model of percolation of electrons in mixed impurity states. The transition point coincides with the percolation threshold of the classically accessible spheres of the impurity states. At this point the energy distribution of the electrons in the impurity band obeys Boltzmann statistics, and the conductivity can be arbitrarily small. The electron degeneracy that sets in just above the transition point makes the conductivity equal to the minimum metallic conductivity, which increases as $n^{2/3}$ as the impurity density n increases. © *1995 American Institute of Physics.*

1. INTRODUCTION

The metal-insulator transition in randomly inhomogeneous media, including doped semiconductors, has long been at the center of interest in the physics of disordered media.[1,2] Metallic conduction in a semiconductor appears or disappears when a threshold donor-impurity density is reached (in the simplest case, in the absence of compensation). The main investigations of this transition have been on silicon doped with phosphorus. Detailed data on the conductivity near the metal-insulator transition point, down to liquid-helium temperatures, had already been obtained at the end of the sixties.[3] In much later experiments the temperature was lowered to 1 mK and the conductivity was observed to undergo an almost discontinuous change at the transition point.[4] This behavior, in general, corresponds to the Mott concept according to which, at $T=0$, the conductivity changes discontinuously at the transition point from the minimum metallic conductivity to zero.[5] However, conductivity values considerably smaller (by three orders of magnitude) than the Mott minimum metallic conductivity were also observed. Thus, the experiment points to a very sharp, but continuous, change of the conductivity at the transition point.

The most popular interpretation of the metal-insulator transition is based on the scaling theory of localization, according to which, at $T=0$, the conductivity vanishes at the transition point as the inverse correlation length. However, the experimental value of the conductivity critical index in Si:P, equal to 0.5 (Ref. 4), is considerably smaller than the theoretical estimates. Extrapolations from opposite sides of the transition point, based on the theories of weak localization and hopping conductivity, give a conductivity critical index close to unity,[2] while numerical analysis of the Anderson model gives 1.5 (Ref. 6). As noted in Ref. 6, the difference between the experimental and theoretical critical indices may be due to the model dependence of this index.[1)] Another possibility is that the observed behavior is not related directly to scaling, since we do not know beforehand in which region of the parameters the correlation length is large.

Usually, the electron gas is assumed to be degenerate up to the metal-insulator transition point, at which the Fermi level intersects the electron-mobility threshold. However, this is not necessarily so if the Fermi energy depends on the proximity to the transition point. For example, in the percolation model of overlapping atoms in gaseous metals, Boltzmann statistics is applicable to the mixed quasiatomic states near the transition point.[8] In this case, the conductivity is determined by the weakly excited electrons near the ground level of the quasiatoms. Although the mobility as a function of the energy of the weakly excited electrons is described in the framework of scaling theory, the energy-averaged conductivity does not have a singularity at the transition point. When, at a somewhat higher density, electron degeneracy sets in, the conductivity becomes equal to the minimum metallic conductivity. Thus, in the percolation model of overlapping atoms, two concepts regarded as alternatives (scaling and minimum metallic conductivity) are combined. By comparison with the scaling theory of the metal-insulator transition, this model is closer to a microscopic model and possesses the advantage of describing the temperature dependence.

In doped semiconductors the analog of the overlapping atoms is the impurity states of the electrons. The fundamental role of percolation in this system and the relation of percolation to the metal-insulator transition are well known.[1] However, the standard analysis is limited to the determination of the transition point, and does not touch upon the problem of mixing of the electron impurity states.

The aim of this article is to apply the percolation model to impurity states in semiconductors in order to describe the low-temperature conductivity in a wide neighborhood of the metal-insulator transition point. Attention is paid principally to the role of electron degeneracy in the mixed impurity states at temperatures close to absolute zero. A simple explanation is given of the well known fact that, irrespective of the degeneracy, the conductivity can sometimes be described approximately by the same formulas as in the Boltzmann case.[9]

The plan of the article is as follows. In Sec. 2 we consider mixed states of impurity-band electrons that are almost coupled to local levels below the bottom of the conduction band of the semiconductor. In Sec. 3 we describe the percolation mobility of electrons in these states, which depends on

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their excitation energy. In Sec. 4 we analyze the dependence of the energy-averaged conductivity on the density of impurity centers and the temperature.

2. MIXED IMPURITY STATES

In a silicon matrix phosphorus forms shallow impurity levels with ionization potential $I \simeq 45.5$ meV (Ref. 9). The electron wave function corresponding to such a level is concentrated mainly within a classically accessible sphere of radius $e^2/\varepsilon I$, where e is the electron charge and $\varepsilon \simeq 11.5$ is the dielectric permittivity of the silicon matrix. The metal-insulator transition occurs at phosphorus density $n = 3.8\times 10^{18}$ cm^{-3} (Ref. 4). As is easily verified, this point coincides with the result found by the Monte Carlo method for the percolation threshold of randomly distributed overlapping spheres[1] playing the role of the classically accessible spheres for the electrons in the impurity levels:

$$\frac{4\pi}{3}(e^2/\varepsilon I)^3 n = 0.34. \tag{1}$$

Since the overlapping impurity states virtually screen each other, the localized states are mixed with free-motion states above the screened potential well. The free-motion energy ε_p is determined by the asymptotic momentum p. By the variational principle of quantum mechanics, as a result of excitation the internal energy of an impurity is always above the isolated-impurity level. Therefore, the minimum internal energy of a screened impurity is

$$E_p = -I + \varepsilon_p. \tag{2}$$

On the other hand, the internal energy of an impurity can be expressed in terms of the energy representation a_{mn} of the density matrix:

$$E_p = a_{00}(-I) + a_{pp}\varepsilon_p, \tag{3}$$

where the diagonal matrix elements a_{00} and a_{pp} correspond to the probabilities of the ground state and of free motion, normalized by the condition

$$a_{00} + a_{pp} = 1. \tag{4}$$

Equations (2)–(4) are compatible if the matrix elements a_{pp} and a_{00} are in the same ratio as the energy of free motion and the binding energy:

$$a_{pp}/a_{00} = \varepsilon_p/I. \tag{5}$$

Hence, weakly excited mixed states, for which $\varepsilon_p \ll I$, are basically similar to the state of an isolated impurity (except for the asymptotic behavior at large distances, which is determined by the small admixture of free motion).

The energy spectrum of the free motion is determined by the structure of the conduction band of the semiconductor. In particular, in the Brillouin zone of silicon there are six equivalent valleys. Near the bottom of a valley the spectrum has the form

$$\varepsilon_p = p_l^2/2m_l + p_t^2/2m_t, \tag{6}$$

where p_l and p_t are, respectively, the longitudinal and transverse components of the momentum, reckoned from the bottom of the valley, and m_l and m_t are the effective electron masses. Applying a frequently used simplification, we shall consider spherical valleys with an effective mass corresponding to the electron density of states: $m = m_l^{1/3} m_t^{2/3} = 0.32 m_e$, where m_e is the free-electron mass.[10]

Since the electrons remain almost localized, they can pass only between neighboring impurities (from an occupied state to a virtual hole). The diffusion coefficient resulting from these random walks is

$$D = l_a^2/3\tau', \tag{7}$$

where $l_a = (4\pi n/3)^{-1/3}$ is the average spacing between impurities and τ' is the average electron-transition time determining the diffusion coefficient.

We shall also express the diffusion coefficient in terms of characteristics of the free motion:

$$D = \tfrac{1}{3} l_a v \vartheta, \quad \vartheta = \tau/\tau', \tag{8}$$

where v is the asymptotic speed of free motion of an electron and $\tau = l_a/v$ is the time of free flight between neighboring impurities. The factor $\vartheta < 1$ appearing in (8) in a product with the minimum gas-kinetic diffusion coefficient determines the degree of localization of the electrons.

Note that, because of the finite transition time, the free motion admixed into the ground state of the impurity is restricted to a certain sphere. The radius of the sphere that can be filled by a diverging wave in the transition time is equal to

$$l' = v\tau'. \tag{9}$$

Since the electron-transition time is greater than the mean free time, l' is greater than the distance between neighboring impurities. The volume of the localization sphere is equal to

$$\Omega = n^{-1}\vartheta^{-3}. \tag{10}$$

The smaller is ϑ, the stronger is the localization, but the volume of the localization sphere is greater as well. This implies that strong localization makes it possible to distinguish impurity states on different centers, even if their localization spheres overlap strongly.

Since the potential of an impurity ion is screened over distances of order l', the density of mixed states corresponds to free motion in the volume Ω. Thus, in comparison with free electrons, the density of electron states per impurity ion increases by a factor of ϑ^{-3}. It follows from this that the Fermi energy is renormalized as follows:

$$\varepsilon_F' = \varepsilon_F \vartheta^2, \tag{11}$$

where ε_F is the Fermi energy of the free electrons in the conduction band.

3. PERCOLATION MOBILITY

As follows from the Einstein relation between the diffusion coefficient and the mobility, the localization factor ϑ renormalizes the average mobility in the same way:

$$\langle \mu_p \rangle = e\tau\vartheta/m. \tag{12}$$

To determine this factor we shall consider transitions of electrons (to virtual holes) between overlapping classically accessible spheres of impurity states. It is obvious that the probability of such transitions depends on the fraction of the volume that is classically accessible at the given energy:

$$\zeta(E_p)=\frac{4\pi}{3}\,(e^2/\varepsilon|E_p|)^3 n. \tag{13}$$

In particular, the mobility should vanish below the energy level determined by the percolation condition

$$\zeta(E_c)=\zeta_c, \quad \zeta_c\simeq 1/3. \tag{14}$$

Using (13) and the condition (14), we easily obtain an expression for the mobility threshold:

$$E_c=-e^2(4\pi n/3\zeta_c)^{1/3}. \tag{15}$$

According to the scaling theory of localization, near the threshold the mobility varies as the inverse correlation length, i.e.,

$$\mu_p \propto (E_p-E_c)^{\nu}, \tag{16}$$

where ν is the critical index of the correlation length. In the case of localization in percolation clusters the index ν is slightly less than 0.9 (Ref. 11), i.e., differs little from unity.

After an almost linear increase above threshold, the dependence of the mobility on the energy saturates (when the larger part of the volume becomes accessible, and the mobility reaches the minimum gas-kinetic value). A characteristic of the corresponding accessible-volume fraction is provided by the packing fraction for random close packing of spheres, approximately equal to 2/3. Thus, saturation occurs near the energy level

$$E_g=-e^2(4\pi n/3\zeta_g)^{1/3}, \quad \zeta_g\simeq 2/3. \tag{17}$$

For the calculations below we use the following schematic representation of the mobility as a function of the energy:

$$\mu_p/\mu_m=\begin{cases} 0, & \varepsilon_p<\Delta_c, \\ (\varepsilon_p-\Delta_c)/(\Delta_g-\Delta_c), & \Delta_c<\varepsilon_p<\Delta_g, \\ 1, & \varepsilon_p>\Delta_g, \end{cases} \tag{18}$$

where $\mu_m=e\tau/m$ is the minimum gas-kinetic mobility, and Δ_c and Δ_g are the characteristic excitation energies, defined by the expression

$$\Delta_i=E_i+I=I-e^2(4\pi n/3\zeta_i)^{1/3}, \quad i=c,g. \tag{19}$$

The averaging over the energy should be performed with a Fermi weight function (which determines the probability that the initial state is occupied and the final state is free)

$$G(\varepsilon_p)=f(\varepsilon_p)[1-f(\varepsilon_p)]=-\partial f/\partial\varepsilon_p, \tag{20}$$

where $f(\varepsilon_p)$ is the Fermi distribution (which makes the second equation in (20) an identity)

$$f(\varepsilon)=[e^{(\varepsilon-\mu)/T}+1]^{-1}, \tag{21}$$

in which μ is the chemical potential of the electrons. Below the metal-insulator transition point, for $\Delta_c\gg T$, the average mobility depends exponentially on the temperature, i.e., corresponds to the Boltzmann limit. Direct calculation gives the localization factor

$$\vartheta=\frac{T(F_c-F_g)}{(\Delta_g-\Delta_c)}\simeq\frac{2}{\sqrt{\pi}}\frac{\sqrt{\Delta_c T}}{\Delta_g-\Delta_c}\exp\left(-\frac{\Delta_c}{T}\right),$$

$$\Delta_g>\Delta_c\gg T, \tag{22}$$

where the functions F_i ($i=c, g$) are combinations of incomplete Γ-functions:

$$F_i=\sqrt{\frac{2}{\pi}}\left[\Gamma\left(\frac{5}{2},\frac{\Delta_i}{T}\right)-\frac{\Delta_i}{T}\Gamma\left(\frac{3}{2},\frac{\Delta_i}{T}\right)\right]$$

$$\simeq\sqrt{\frac{2}{\pi}}\sqrt{\frac{\Delta_i}{T}}\exp\left(-\frac{\Delta_i}{T}\right), \quad \Delta_i\gg T.$$

Above the transition point the mobility threshold appears only as a virtual threshold ($\Delta_c<0$). In the Boltzmann approximation we have

$$\vartheta=\frac{3T/2-\Delta_c-TF_g}{\Delta_g-\Delta_c}\simeq\frac{3T/2-\Delta_c}{\Delta_g-\Delta_c}, \quad \Delta_c\leqslant 0,$$

$$T\ll\Delta_g. \tag{23}$$

In the general case the averaging in (18) gives

$$\vartheta\simeq\begin{cases} (\langle\varepsilon_p\rangle-\Delta_c)/(\Delta_g-\Delta_c), & \langle\varepsilon_p\rangle<\Delta_g, \\ 1, & \langle\varepsilon_p\rangle>\Delta_g, \end{cases} \tag{24}$$

where $\langle\varepsilon_p\rangle$ is the energy averaged with the Fermi weight function (20). In the limiting cases this energy is equal to ε_F' if $\varepsilon_F'\gg T$, or $3T/2$ if $\varepsilon_F'\ll T$. In the intermediate case we use the interpolation formula

$$\langle\varepsilon_p\rangle=\varepsilon_F'+3T/2. \tag{25}$$

Substituting Eq. (25) into (24) and taking Eq. (11) into account, we obtain for the localization factor an implicit expression that is essentially an equation:

$$\vartheta=\begin{cases} (\varepsilon_F\vartheta^2+3T/2-\Delta_c)/(\Delta_g-\Delta_c) & \text{if this is } <1, \\ 1, & \text{otherwise.} \end{cases} \tag{26}$$

The case $\vartheta\to 0$ corresponds to the Boltzmann limit (23). We note that at the metal-insulator transition point the Boltzmann limit exists even for $T\to 0$. In fact, at this point ($\Delta_c=0$) it follows from (23) that $\vartheta\propto T/\Delta_g$, and, consequently, the ratio of the renormalized Fermi energy to the temperature tends to zero:

$$\varepsilon_F'/T\propto\varepsilon_F T/\Delta_g^2\to 0 \quad (T\to 0), \tag{27}$$

which is the condition for the applicability of Boltzmann statistics.

In general, Eq. (26) can have three roots, of which only one has the indicated Boltzmann limit as the density is decreased. Of the other two roots, one is unstable and the second is $\vartheta=1$. Above a certain density the root that has the Boltzmann limit vanishes, and a discontinuous transition to the point $\vartheta=1$ occurs. This density above which the electrons are always degenerate at low temperatures is determined by the condition

$$\frac{(3T/2-\Delta_c)\varepsilon_F}{(\Delta_g-\Delta_c)^2}=\frac{1}{4}. \tag{28}$$

We note that the localization-factor discontinuity associated with the electron degeneracy is not reflected in the conductivity, since this factor cancels (see below). For the same reason, there is no need here to write out the explicit solution of Eq. (26) for the case of degeneracy.

4. THE CONDUCTIVITY

In the metallic state, one electron per impurity atom gives a contribution to the conductivity, and, therefore,

$$\sigma = en\langle\mu_p\rangle = e^2\tau\vartheta n/m. \tag{29}$$

This expression is none other than a modified Drude formula, including an extra factor that takes the electron localization into account. In the Boltzmann case the minimum mean free time is equal to

$$\tau = l_a/v_T, \tag{30}$$

where $v_T = \sqrt{8T/\pi m}$ is the thermal average speed of the electrons. Note that in the presence of the localization factor the conductivity has no lower bound; in other words, a minimum metallic conductivity does not exist.

In the case of degeneracy, however, the collision time is inversely proportional to the (renormalized) Fermi velocity:

$$\tau = l_a/v_F', \quad v_F' = v_F\vartheta. \tag{31}$$

Consequently, the factor ϑ in the Drude formula (29) cancels, so that the conductivity is equal to the minimum conductivity with a mean free path coinciding with the spacing between impurities:

$$\sigma = e^2 l_a n/p_F. \tag{32}$$

We recall that, by virtue of the relation (27), degeneracy is possible not at the metal-insulator transition point itself but only on the metallic side of this transition.

However, the range of applicability of Eq. (32) is found to be limited, because with increasing impurity density, when the localization factor tends to unity, the electrons become almost free. In this case the mean free path can exceed the spacing between the impurities. In fact, the minimum mean free path is limited by the uncertainty principle:[12]

$$l \sim \hbar/\Delta p, \tag{33}$$

where Δp is the uncertainty of the electron momentum. At sufficiently high temperatures we have $\Delta p \sim mv_T$, so that the minimum mean free path of an electron is of the order of its thermal wavelength. In the case of degeneracy, taking as the energy uncertainty the geometric mean of the Fermi energy and the temperature, we have

$$\Delta\varepsilon \sim p_F\Delta p/m \sim \sqrt{T\varepsilon_F}, \tag{34}$$

whence we again obtain $\Delta p \sim \sqrt{mT}$ (this estimate makes sense if the ratio of the Fermi momentum to the thermal momentum is not too large—say, not greater than 10). Thus, in the case of not too low temperatures, the minimum electron mean free path is give by the thermal wavelength:

$$l = \hbar/mv_T, \quad v_T > \gamma v_F, \tag{35}$$

while for sufficiently low temperatures it is determined by the inverse Fermi wave vector:

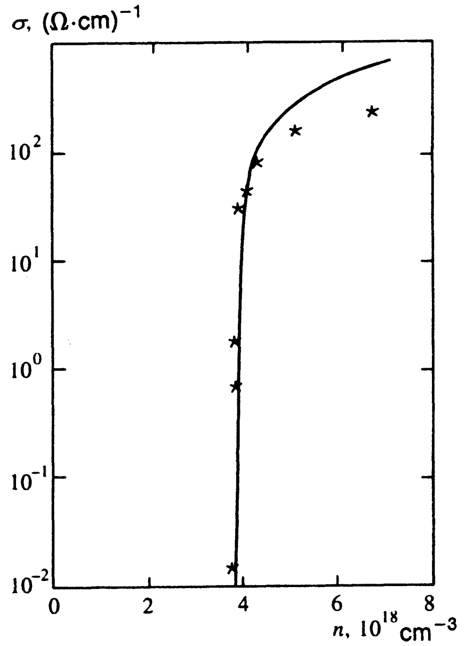

FIG. 1. Metal-insulator transition in Si:P. The solid curve is the theoretical calculation for $T \to 0$; the points are experimental data from Ref. 4.

$$l = \hbar/\gamma m v_F, \quad v_T < \gamma v_F. \tag{36}$$

Here, $\gamma \sim 0.1$ is a small parameter that corresponds to matching of Eqs. (35) and (36) at $v_T = \gamma v_F$. At not too low temperatures ($v_T > \gamma v_F$), the collision time amounts to

$$\tau \simeq \hbar/m v_T v_F \approx l_a/v_T. \tag{37}$$

In this equality the inverse Fermi wave vector can be expressed in terms of the spacing between impurities by means of the formula (which takes into account the presence of six valleys)

$$\hbar/mv_F = (\pi^2 n/2)^{-1/3}. \tag{38}$$

Equation (37) can be understood as suggesting the possibility of applying Boltzmann statistics, in which case the mean free time has the same form [in fact, this possibility is well known in the case of pure metals when the ratio of the Fermi energy to the temperature is of the order of 10^2 (Ref. 9)]. Because of this coincidence, the modified Drude formula in the Boltzmann approximation can be used as an interpolation formula in the case of electron degeneracy as well. In this case, not to close to the transition point, the conductivity has a power dependence:

$$\sigma \propto n^{2/3}, \quad p_T > \gamma p_F. \tag{39}$$

In the case of very low temperatures the minimum mean free path is determined by the inverse Fermi wave vector in accordance with Eq. (36), and the dependence of the conductivity on the density far from the transition point is then weaker:

$$\sigma \propto n^{1/3}, \quad p_T < \gamma p_F. \tag{40}$$

The conductivity calculations (Figs. 1–3) were carried out using the modified Drude formula with the Boltzmann

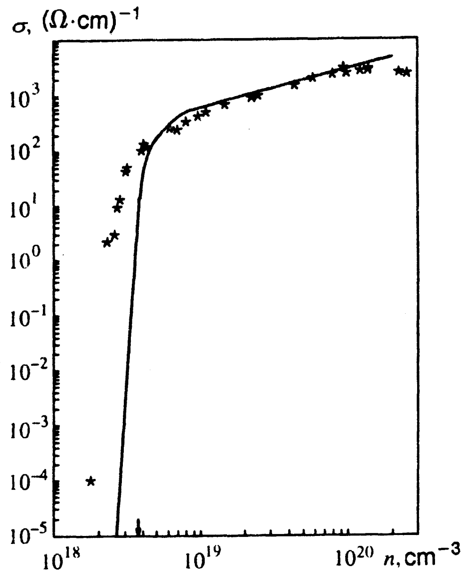

FIG. 2. Dependence of the conductivity of Si:P at $T=4.2$ K on the density of phosphorus. The metal-insulator transition point is indicated by an arrow. The solid curve is from the theory, and the points are from the experiment of Ref. 3.

localization factor (22), (23), expressed in terms of incomplete Γ-functions, and the mean free time was estimated with allowance for the degeneracy. The effective mass was taken equal to the free-electron mass. To match the different expressions for the minimum mean free path the parameter value $\gamma = 0.1$ was used.

For $T \to 0$ (Fig. 1) the conductivity below the metal-insulator transition point (and at this point) vanishes, while above this point (on a logarithmic scale) the conductivity increases practically discontinuously, in agreement with the experimental data of Ref. 4. We note that the critical index of the conductivity in the model under consideration is equal to unity, since a linear dependence of the percolation mobility on the energy above threshold is assumed. A more detailed description of the percolation mobility requires a considerably deeper analysis.

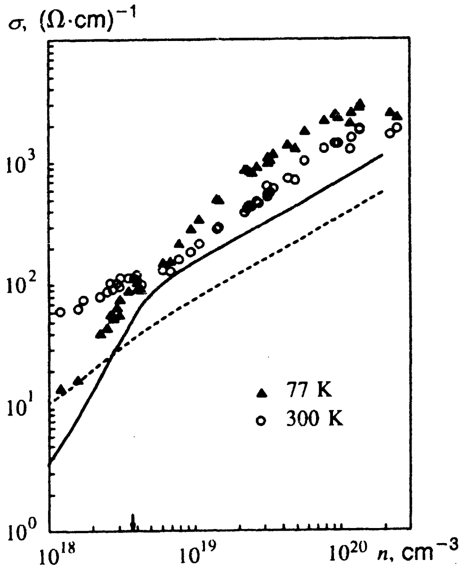

FIG. 3. The same as in Fig. 2, but at $T=77$ K (the solid curve) and $T=300$ K (the dashed curve).

The dependence of the conductivity on the density at higher temperatures is shown in Figs. 2 and 3. At liquid-helium temperature and above, in almost the entire range of phosphorus densities of interest, the electron mean free path is given by the thermal wavelength, so that the mean free time coincides with the Boltzmann formula (37). We note that the theory agrees qualitatively with the experimental data even when the density dependence of the conductivity is very strong.

5. CONCLUSION

In doped semiconductors the metal-insulator transition associated with the percolation of electrons in shallow impurity levels has the same nature as the corresponding transition in gaseous metals. Despite the large differences between these systems, at temperatures differing by a factor of a thousand, their conductivity is qualitatively described by universal formulas. The distinctive features of the electronic properties near the metal-insulator transition are due to mixing of states as a consequence of mutual screening of impurities. Degeneracy of the electrons in the mixed states is possible only above the percolation threshold, and near the threshold Boltzmann statistics is always applicable. For $T \to 0$, averaging of the scaling dependence of the electron mobility on the excitation energy over the Boltzmann distribution gives a practically discontinuous change of the logarithm of the conductivity at the metal-insulator transition point, and this transition becomes more and more smeared out with increase of temperature.

For the degenerate electron gas above the metal-insulator transition point a Mott minimum metallic conductivity exists. In the case when the electron mean free path is determined by the thermal wavelength, the minimum conductivity increases with impurity density as $n^{2/3}$. Near absolute zero temperature the minimum electron mean free path is a multiple of the inverse Fermi wave vector, and the minimum conductivity is proportional to $n^{1/3}$.

In contrast to gaseous metals in the vicinity of the liquid-gas critical point, in the impurity subsystem of a semiconductor there is no phase transition, and this makes it possible to study the metal-insulator transition at very low temperatures. The importance of these investigations is considerably enhanced because of the universal percolation mechanism of this transition.

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[1] The experimental index depends in turn on the neighborhood (of the transition point) chosen for its determination (see the critical discussion in Ref. 7 and the references therein).

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