

STRUCTURE OF IMPURITY BAND AND HOPPING CONDUCTION

A.L. Efros and B.I. Shklovskii

A.F. Ioffe Physical-Technical Institute
Academy of Sciences of the USSR, Leningrad
U S S R

The results of recent Monte-Carlo simulation of the impurity band structure and related phenomena in doped semiconductors are reviewed

If the thermal energy kT is smaller than the width of the impurity band, the electronic properties of semiconductors such as temperature dependence of the hopping and band conduction, and the linewidth of intrainpurity absorption are determined by the impurity band structure. In this talk we report the results of Monte-Carlo computer simulation of the impurity band and a quantitative study of the above physical phenomena [1-7]. For definiteness, we consider an n-type compensated semiconductor where all acceptors are negatively charged, donors are partly ionized and positively charged and partly occupied and neutral. If the donor concentration N_D is so small that the mean distance between impurities is much larger than the effective Bohr radius a , all the donor states are localized. Then the donor levels are shifted mainly by the Coulomb potentials of randomly distributed charge impurities and the shift is classical, i.e. it is equal to the potential created on a given donor. Such a system we call "a classical impurity band". The model works well if $N_D \leq 0.1 N_M$ where N_M is the Mott transition concentration.

At low temperatures the description of spatial distribution of ionized and neutral donors and the energy structure of the classical impurity band is a rather complicated many-electron problem which can be reduced to minimization of the total electrostatic energy of the system

$$H = \frac{e^2}{\epsilon} \left[\frac{1}{2} \sum_{i,j} \frac{(1-n_i)(1-n_j)}{r_{ij}} - \sum_{i,v} \frac{1-n_i}{r_{iv}} + \frac{1}{2} \sum_{v \neq v'} \frac{1}{r_{vv'}} \right] \quad (1)$$

where e is the electronic charge, ϵ is the lattice dielectric constant, $r_{ij} = |r_i - r_j|$, r_i , r_j are the donor coordinates, and r_{iv} , $r_{v'v''}$ are the acceptor ones. The occupation number $n_i = 1$ if the donor i is occupied by an electron and $n_i = 0$, if it is ionized. One has to find set $\{n_i\}$ minimizing the total energy H for a given total number of electrons and the set $\{\epsilon_i\}$ of one-electron energies

$$\epsilon_i = \frac{e^2}{\epsilon} \left[\sum_v \frac{1}{r_{vi}} - \sum_{j \neq i} \frac{1-n_j}{r_{ij}} \right] \quad (2)$$

ϵ_i is the potential created on the donor i by all other charges of the system. The problem has been solved by Monte-Carlo computer simulation (The program is described in details in [1,7]).

A pseudo-random number generator gives N donor and KN acceptor coordinates within a cube. N ranges from 100 to 1600 at 12 different K from 0.01 to 0.98. $N(1-K)$ electrons are randomly distributed between the donors and minimization of eq.(1) is made with respect to all one-electron transitions. It leads to so-called pseudoground states. At $N \leq 400$ we are able to choose a true ground state among them and to check up that there is no difference between the properties of the ground and the pseudoground states. Therefore we use only pseudoground states to obtain the density of states (DS), Fermi level μ and other quantities. All of them are averaged over 200-15 different sets of impurity coordinates at N from 100 to 1600. Averaged values are extrapolated to $N = \infty$. The dependence $\mu(K)$ has been found to be in agreement with the theoretical predictions at $K \ll 1$ and at $1 - K \ll 1$ [2,8].

The most important features of the DS (Fig.1) are the two-peak structure predicted by Pollak and Knotek [9,10] and a soft Coulomb gap in the vicinity of the Fermi level [11]. In this region the computer results for the DS can be fitted into the law

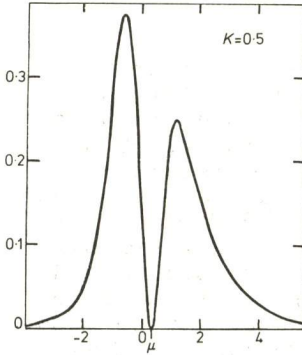


Fig.(1) Normalized DS plotted against energy $\mathcal{E}$ at $K = 0.5$: Here and below the unit of energy is $e^2 N_D^{1/3} / \alpha$.

$$g(\mathcal{E}) = \alpha_3 (\mathcal{E} - \mu)^2 \quad (3)$$

at $0.15 \leq |\mathcal{E} - \mu| \leq 0.5$ (We use the units $e^2 N_D^{1/3} / \alpha$ for all energies below). We cannot study the region $|\mathcal{E} - \mu| \leq 0.15$ due to a large size effect. It is a long-range interaction which is responsible for the Coulomb gap. So the size effect increases at small $|\mathcal{E} - \mu|$. The constant $\alpha_3 \approx 1$ which agrees with the selfconsistent equation [1].

Stark Broadening of an Intraimpurity Absorption Line

To describe this effect a random spatial distribution of charged impurities is usually assumed. But actually at $kT < e^2 N_D^{1/3} / \alpha$ the distribution is close to that in the ground state and is strongly correlated. Distribution of electric fields on neutral donors in the ground state is computed in [4], and the characteristic field is shown to be much smaller than at random distribution and to increase faster with compensation.

Concentration and Compensation Dependences of the Impurity to Band Activation Energy $\mathcal{E}_1$

The bottom of the conduction band is bent by the potential of charged impurities. Therefore the band electron conductivity is determined by the electrons whose energies are larger than the percolation level V_p . So the activation energy $\mathcal{E}_1 = E_0 - \mu + V_p$ where E_0 is the binding energy of a single donor. The percolation level V_p is computed [6] using the stored spatial distribution of charged impurities and results are shown in Fig.(2) by full line together with other theoretical results [12-14] and experimental data [15-16]. At strong compensation our theory fits well the experimental points. At intermediate compensation the variation of $\mathcal{E}_1$ becomes of the order of kT . It makes difficult the comparison of the theory and experiment.

Temperature Dependence of the Hopping Conduction [5, 3]

In the case of neighbour hopping the resistivity has a form $\rho = \rho_3 \exp(\epsilon_3 / \kappa T)$. To treat the problem theoretically one has to solve the percolation problem with the bonding criterion [8].

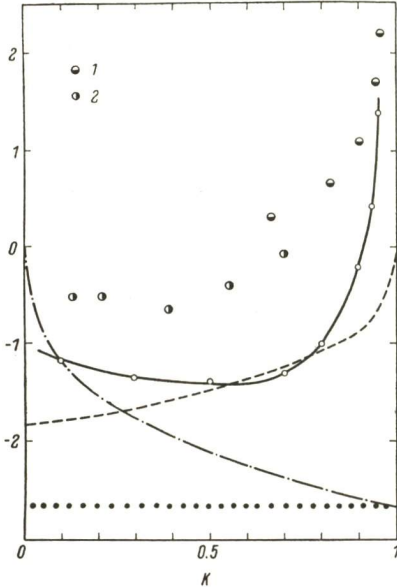


Fig. (2) $\epsilon_i - E_0$ plotted against the compensation degree K : The experimental data are taken from [15] (1) and [16] (2). Theoretical results: [6] (full line), [12] (dotted line), [13] (chain line).

es the shift of the percolation threshold due to small variation of the bonding criterion. If one neglects the second term in eq. (4), the percolation threshold $\xi_c^0 = 2 r_c / a$, where $r_c = 0.865 N_D^{-1/3}$.

In the first order of the percolation theory the result is

$$\xi_c - \xi_c^0 = \frac{\epsilon_p}{\kappa T}, \quad \epsilon_p = \langle \epsilon_{ij} \rangle \quad (7)$$

where angular brackets mean averaging over all pairs of donors with r_{ij} which are close to r_c . In this approximation ϵ_p is the activation energy ϵ_3 . It has been computed using eq. (4), eq. (7) and the sets of $\{r_{ij}\}$, $\{\epsilon_{ij}\}$ and $\{n_{ij}\}$ corresponding to the ground state. The results are shown by curve 1 in Fig. (3A). They drastically contradict to experimental data.

One can rewrite eq. (4) in dimensionless variables and define the function $\chi_c = N_D^{1/3} \xi_c a / 2$ which depends only on t and K .

We have computed this function in a wide range of t and K . For this purpose a new block has been added to the minimization program. It finds the threshold χ_c of the percolation between two opposite faces of the cube, using criterion eq. (4) and the coordinates and energies computed in the first part of the program. At $t^{-1} \leq 0.05$ the result is

$$\frac{2z_{ij}}{a} + \frac{\epsilon_{ij}}{\kappa T} \leq \xi \quad (4)$$

$$\epsilon_{ij} = \begin{cases} \epsilon_i - \epsilon_j - e^2 / 2z_{ij} & \text{at } (\epsilon_i - \mu)(\epsilon_j - \mu) < 0 \\ \max \{ |\epsilon_i - \mu|, |\epsilon_j - \mu| \} & \text{otherwise} \end{cases} \quad (5)$$

Then $\rho = \rho_0 \exp \xi_c$ where ξ_c is the percolation threshold, and ρ_0 is a prefactor. The nearest neighbour hopping occurs if dimensionless temperature

$$t = \frac{\kappa T a}{e^2 N_D^{1/3}} \frac{2}{N_D^{1/3} a} \quad (6)$$

is larger than unity. Then the typical value of the second term in eq. (4) is smaller than the first one.

If $t \gg 1$, the percolation perturbation theory can be used [8]. It gives

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$$\eta_c = 0.865 + \eta_p t^{-1} \quad (8)$$

The perturbation theory gives $\eta_p = \epsilon_p \alpha / e^2 N_D^{1/3}$ where ϵ_p is defined by eq.(7), and we have checked up that η_p and ϵ_p are in a good agreement. The most peculiar point is that eq.(8) has been valid only within a very narrow region of $t^{-1} \leq 0.05$, and that the plot $\eta_c(t^{-1})$ has another linear region

$$\eta_c = 0.865 + \tilde{\eta}(K) + \eta_K t^{-1} \quad (9)$$

at $0.15 \leq t^{-1} \leq 0.5$ with a quite different slope η_K and with a shift $\tilde{\eta}(K)$ increasing with K. Usually eq.(9) is valid in all the temperature range where nearest neighbor hopping is observed.

In n-Ge, for example, with Sb concentration $N_D = 3 \cdot 10^{15} \text{ cm}^{-3}$ it covers the temperature range from 1.3 K to 4.3 K. The perturbation theory region relates to higher temperatures where usually the band conduction dominates. So the activation energy is rather

$\epsilon_K = \eta_K e^2 N_D^{1/3} / \alpha$ than ϵ_p . It is shown by curve 2 in Fig.(3A) to be much closer to the experimental data.

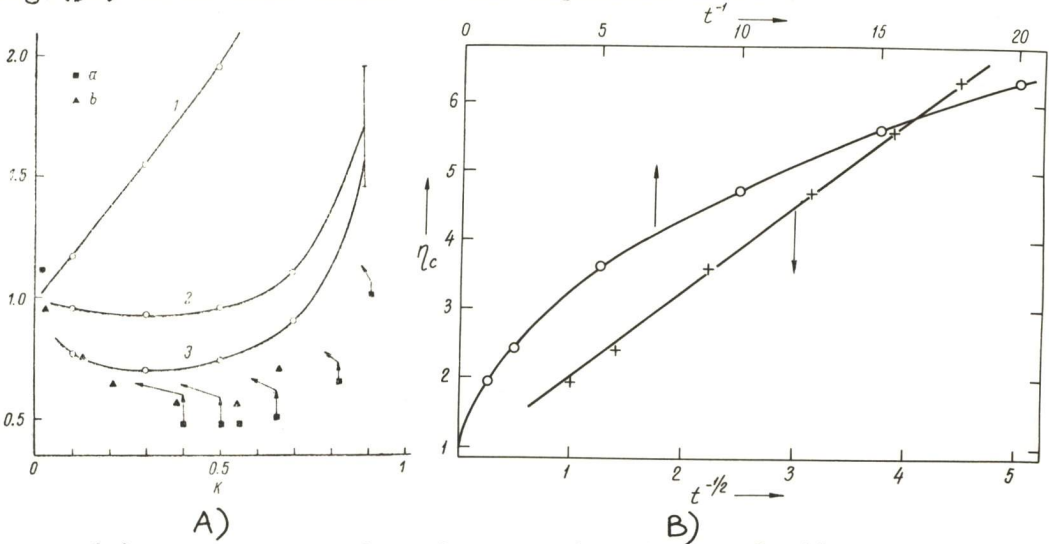


Fig.(3). Temperature dependence of hopping conduction

A) Theoretical and experimental values of ϵ_3 plotted against K.

Theoretical results: ϵ_p (1), ϵ_K (2), final result (3).

Experimental data: p-Ge [17] (a), n-Ge [16] (b)

B) η_c against $t^{-1/2}$ and t^{-1} for the variable range hopping

The difference between the theoretical and experimental values of ϵ_3 can be diminished if one takes into account so called "adiabatic" processes, as has been suggested by Knotek and Pollak [10]. It means that an electron hops in time intervals when the occupations of some other sites differ from those of the ground state in such a way that an extra potential created by the sites decreases the activation energy of the first electron. The search for such combination has been included in the percolation part of the program, and the results are shown by curve 3 in Fig.(3A). The vertical arrows in Fig.(3A) show the extrapolation of the experimental points to the purely classical case $\alpha \rightarrow 0$ which is rather

arbitrary at $K > 0.4$. The inclined arrows relate to the corrections in the parameters of the p-Ge samples, as proposed in [18]. One can see that the agreement between the theoretical and experimental values is satisfactory at least at $K \leq 0.7$. The theoretical value at $K = 0.9$ has a small accuracy due to a large finite size effect.

It is interesting that the term $\tilde{\eta}(K)$ in eq.(9) leads to a slight increase of ρ_3 with increasing compensation, which has been observed experimentally [16].

The same program has been used to compute the percolation threshold ξ_c at low temperatures $t \ll 1$ where variable range hopping occurs. Only one compensation $K = 0.5$ has been studied. The result is given in Fig.(3B). One can see that the resistivity obeys the law

$$\rho \sim \exp\left(\frac{T_0}{T}\right)^{1/2}, \quad T_0 = \frac{\beta e^2}{2a} \quad (10)$$

predicted earlier [11]. The numerical factor β , as obtained from Fig.(3B), is equal to 2.8. The difference between eq.(10) and the well-known Mott's law is due to the Coulomb gap in the DS (see eq.(3)).

Mott [19] and Pollak [20] criticized eq.(10). Their main point is that the low temperature hopping has a many-electron character. The potential of an electron on the site A (Fig.(4)) creates a correlation of the occupation numbers of neighbouring sites and a polarization around the site A. So it forms a kind of polaron. The hop of the electron from A to B is accompanied by reconstruction of the polaronic clouds around both sites. Mott and Pollak suggest that there is no Coulomb gap for such hops of polaron, that DS of polarons is constant, and the Mott law is valid. (Pollak [20] has proposed recently a many-electron cascade hopping which gives the exponent in the temperature dependence even smaller than $1/4$). We disagree with them in the following points:

(i) We have studied independently the polaronic transport [21,22] and argued that the polaronic atmosphere can be considered as a renormalization of the dielectric constant. Then the eq.(3) can be derived for the DS of the polarons in the same way as for the DS of the one-electron excitations. This leads to eq.(10) for the resistivity. Our arguments can be formulated also in another way. Let ω be the energy of the polaron transition from A to B and R be the hop distance. The parameters of pairs contributing to the Mott law obey the relation $\omega R^3 = \text{const}$ where $\omega \rightarrow 0$ and $R \rightarrow \infty$ as $T \rightarrow 0$. It is important also that the distance between neighbouring pairs should be of the order of R , otherwise they do not contribute to d.c. conduction. Suppose that we excite two such pairs simultaneously. The work $2\omega + E_{\text{int}}$ is necessary, where the interaction energy of pairs $E_{\text{int}} = \alpha e^2/\epsilon R$ and the factor α can be negative. Using the Mott relation $\omega R^3 = \text{const}$, one finds that

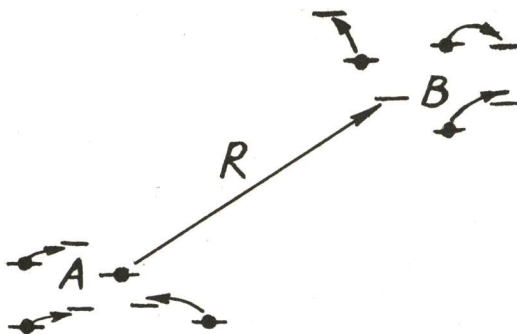


Fig.(4). Transition of polaron

$e^2/\kappa R \gg \omega$ as $T \rightarrow 0$. It means that the ground state is unstable with respect to simultaneous creation of the two pairs. It means in fact that in the true ground state the distance between such pairs is much larger than R and they cannot contribute to the d.c. conduction. Only the relation $\omega R = \text{const.}$ is selfconsistent and it gives eg.(10). It is not essential in the above consideration whether we are speaking about one-electron excitations or about polarons. Only the charge of an excitation is important [22]. For one-electron excitations these arguments have been checked up by the Monte-Carlo simulation reported here. So we hope they are valid for polarons as well.

(ii) We believe that the above discussion is essential only for extremely low temperatures, while in the region accessible to the Monte-Carlo simulation ($|\epsilon - \mu| > 0.15$) many-electron hopping is not very important. The arguments are as follows: The polaronic effect has to give an exponential fall of the DS [22] but we observe a soft gap. Also we do not observe any difference between the DS averaged over pseudoground states and true ground state. The preparation of the pseudoground state includes minimization with respect to one-electron transitions only, while the exponential fall should be the result of many-electron minimization. So this last step is apparently of no importance. Therefore we believe that the computation of resistivity in terms of one-electron hopping discussed above is a good approximation in the temperature range under study. (In fact, the experiments at lower temperatures are very difficult to make because resistivity becomes very large).

Unfortunately, the experimental data on the variable range hopping in crystalline semiconductors are rather uncertain. The detailed analysis made by Zabrodskii [23] confirms rather eq.(10) than the Mott law. (See also [8]). On the other hand, since the well-known experiments in MNOS devices support Mott's theory, the situation is not quite clear.

We believe that the minimization program reported here will be useful for some other applications. For example, we are studying now the density of low-energy pair excitations important for low-temperature a.c. conduction and specific heat. The other application considered by our group is two-dimensional impurity band of Na-doped MOS-structure. The electron-electron interaction leads to the interesting peculiarities of the apparent DS obtained by conventional methods. Namely it can be very large and even negative.

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