THE INFLUENCE OF THE COMPENSATION ON THE DENSITY OF IMPURITY STATES AND THE ELECTRIC CONDUCTIVITY OF CRYSTALLINE SEMICONDUCTORS OF DOPED Ge AT HIGH CONCENTRATIONS OF THE DONORS

ĽUDOVÍT HORŇANSKÝ*, Bratislava

The approach of Matsubara and Kaneyoshi [1] to the calculation of the impurity band conduction and the density of states is applied in the situation when diagonal matrix elements of the Hamiltonian have different values, i.e. the potential energy of the electron is fluctuating from place to place. By an approximate solution of the simplified model the influence of the compensation on the density of the impurity states and the conductivity at 0 °K are outlined.

I. INTRODUCTION

Allen and Adkins [2] report in their work that by doping germanium and antimony at a low concentration of donors, a system of donors' levels with coupled states originates the energy of which is about 9.7 meV below the conduction band. With a growing concentration, the overlap between the adjacent states and the accidental position of the adjacent centres causes the energy of the bound states to expand. After the addition of acceptors into the sample, some donors will become ionized. Ionized donors and acceptors (acceptors are all ionized), create Coulomb centres and cause relative great changes in the energy of the adjacent states. This increases further the width of the band.

At low donor concentrations the conductivity is realized by a jump of electrons from the occupied to the unoccupied donor state. Let us consider a semi-conductor with N_D donors and N_A acceptors, $N_D > N_A$ (n-type). At a low temperature, the acceptors will compensate N_A donors and consequently the system will consist of N_A ionized donors, N_A ionized acceptors and $N_D - N_A$ electrons remaining in the donor states. If one of the $N_D - N_A$ donored electrons is near to one of the N_A vacant donored places, it can jump over

to an accessible place, the jump being accompanied by the emission or the absorption of a phonon. The electron cannot jump over to an already occupied place, owing to a large electrostatic energy connected with a double occupation. (The singly occupied states are separated from the doubly occupied ones by the Hubbard energy gap). Miller and Abrahams [3] report in their work that the concentration of donors, under which this model is convenient, is approx. 6×10^{16} cm^{-3} at the n-type Ge and 2×10^{17} cm^{-3} for the n-type of Si.

At a high concentration of donors, the owerlap between the adjacent donors is becoming sufficiently great to enable the Mott-transition to metallic states. Owing to the spin degeneration, the resulting band in the non-compensated material is full only in the lower half, and the activated energy for conduction is not required. Even if the states in the middle of the band will be metallic ones, we can expect that the ones in tails, where the density of states is lower, will still be localized. By an increasing compensation, the Fermi energy E_F is moving towards the region of the localized states and the conduction at a sufficiently great compensation will again require activation. At a very low temperature when kT is much lower than the width of the impurity band, we can expect a transition from metallic conductivity to the "variable hopping régime", where the resistance in the temperature T dependence is expressed by the relation of $\varrho = B \exp (A/T^{1/4})$.

With a growing compensation random potentials will result, principally from the ionized donors and acceptors, the consequence of which is an increase of width of the impurity band. However the density of the states will decrease and the final consequence is the increase of localization. States can then be localized in the Anderson sense.

The influence of the electron correlation, compensation, E_F position in the impurity band etc. on the impurity band conduction of the n-type Ge, are analyzed also by Matsubara and Toyozawa [4] (in the following M-T). They distinguish three basic regions of donor concentrations in which some effects are essential: the region of low concentrations ($< 10^{16}$ cm^{-3}), the region of high concentrations (from 10^{17} cm^{-3} to 10^{18} cm^{-3}), and that of very high concentrations ($> 10^{18}$ cm^{-3}).

In this work we will study the region of the "high concentration of donors", i.e. N_D will be between the intervals 10^{17} to 10^{18} of impurities in a sample of 1 cm^3. As M-T state, it is possible to suppose in agreement with experimental results that in this case in the n-type Ge, carriers move in the so-called impurity band without serious effects of correlation.

* Katedra všeobecnej fyziky PFUK, Mlynská dolina, 816 31 BRATISLAVA, Czechoslovakia.

II. TAKING INTO ACCOUNT THE ACCEPTOR INFLUENCE

In solving the density of the impurity states problem and the metallic conductivity in the donor band, we will use the work of Matsubara and Kaneyoshi [1] as our starting point (in the following M-K only) as well as the work of M-T. In their model, they neglect the influence of the conductivity band and the excited states of impurities. In the construction of the Hamiltonian, the electron correlation and the spin of the electron are also neglected.

The relevant factor for the determination of the state density and conductivity is the accidental character of the impurities arrangement. As the authors M-K and M-T themselves report, their approach enables them to view the movement of carriers from donor to donor not as a separate elementary process, but to consider the correlation with the preceding and the subsequent junctions.

Let us suppose in the following part that the electron moves in the field of charged centres (donors and acceptors) and in effective field of the rest of electrons so that movement is considerably influenced only by the impurity D, in the immediate environment of which the electron is situated, and the nearest impurity of the adjacent impurity D. We neglect the action of the rest of the impurities and electrons. The Hamiltonian H in a closer bond approximation can be written in the following form

$$H = \sum_{\{n\}} v_n a_n^* a_n + \sum\sum_{\{m\} \neq \{n\}} V'_{mn} a_m^* a_n . \qquad (1)$$

The matrix elements v_n and V'_{mn} will be considered at most in a double-centre approximation, i.e. we are considering integrals having the atomic functions and potentials centred at most on two different donors.

If we consider the wave functions φ_m of the basic state (1s state) and the potential energy of the electron in the field of the donor centre V_i^D or the acceptor centre V_j^A, respectively, $\varphi_m = (a^3/\pi)^{1/2} \exp(-a|r - R_m|)$, $V_i^D = -V_0(a|r - R_i|)^{-1}$, $V_i^A = -V_0(-a|r - R_i|)^{-1}$ — where $|V_0|$ is the double of the ionized energy $|E_0|$ (owing to the bottom of the conduction band) of the electron in the 1s state described by the function φ_m, a^{-1} is the radius 1s of the orbital, R_i or R_j, respectively, are the position vectors of the admixtured ions — we can express the matrix elements v_n and V'_{mn} in the form:

$$v_n = V_0(1/2 \pm (a^{-1}/R - \exp(-2R/a^{-1})(1 + a^{-1}/R))) = E_0 \pm w(R)$$

$$V'_{mn} = V_0(3/2(1 + aR)\exp(-aR) + ((aR)^2/6)\exp(-aR)), \qquad (2)$$

where the $+$ sign is valid if in the distance R from the donor D there is a donor,

and the $-$ sign if there is an acceptor in the vicinity. The Fourier coefficients of the function development V'_{mn}, which we need in the following are:

$$V_k = \Omega_0^{-1} 64\pi V_0 a^3/(k^2 + a^2)^3 - \Omega_0^{-1} 32\pi V_0 a^5/((k^2 + a^2)^4 . \qquad (3)$$

Let us denote by N_D the number of donors in the system, by N_A the number of acceptors, and by the quotient $K = N_A/N_D$ we will understand the compensation. Owing to a random distribution of impurities (we do not consider any correlations between distributed donors and acceptors), and considering the probability that in the nearest vicinity of the donor centre D there is an acceptor or donor, we can write:

$$p_A = N_A/(N_A + N_D) = K/(1 + K)$$

$$p_D = N_D/(N_A + N_D) = 1/(1 + K).$$

Let us consider the same system of random impurities by distributed impurities. We can suppose that this system has N_D different distributed impurities. Since the distance of the nearest impurity from the given donor centre D may take the value from the interval $(0, \infty)$, the diagonal elements w_n (2) take the values from the interval $(E_0 - V_0, E_0 + V_0)$. However, the distribution of the diagonal values in this interval will be different for each system (with the same N_D and N_A). The part $K/(1 + K)$ of these values belongs to the donors with adjacent acceptors. Consequently we get $N_D K/(1 + K)$ and $N_D/(1 + K)$ of different diagonal values w_n from the interval $(E_0, E_0 - V_0)$, and $(E_0, E_0 + V_0)$. Let us suppose further that the probability of finding the nearest vicinity at a distance between R to $R + dR$ is given by the approximation

$$p(R)\, dR = 4\pi R^2 N' \exp(-4\pi R^3 N'/3)\, dR,$$

where $N' = N_D + N_A$; supposing the independence of the probabilities $p(R)$ and p_A, or $p(R)$ and p_D, respectively, for the probability of the realization of the diagonal value $w_n^+(R)$ (donor vicinity)

$$w_n^+(R) = E_0 + w(R)$$

we can write

$$p^+ = p_D p(R)\, dR$$

and for the probability of finding the diagonal value $w^-(R)$ (acceptor vicinity)

$$w_k^-(R) = E_0 - w(R)$$

we have

$$p^- = p_A p(R)\, dR.$$

Applying the results of the $M - K$ work, we can write for a disordered system, like the one discussed above, the following system of equations:

$$E - E_0 - i\varepsilon = x + \bar{V}, \quad \varepsilon \to 0 \qquad (5)$$

where

$$\alpha = N_D(1 + K)^{-1}\{\int_0^\infty dR\, p(R)(x - w(R))^{-1} + K\int_0^\infty dR\, p(R)(x + w(R))^{-1}\}, \qquad (6)$$

where

$$\bar{V} = \sum_\kappa V_\kappa/(1 - \alpha V_\kappa)$$

and V_κ are the Fourrier coefficients of the matrix element V'_{mn}. With the help of the solution α of this system, we can express the density of the states and the conductivity averaged over a random decomposition of admixtures.

III. SIMPLIFIED SOLUTION

In this part the simplified approximate solution of the problem is given — the influence of the compensation on the course of the state density $D(E)$ and the conductivity σ at $T = 0\,^\circ\text{K}$.

Let us consider only the existence of two different diagonal values, w_D and w_A, which correspond to the maximum function $p(R)$ (4). If the maximum is realized for $R = \bar{R}$, from (2) it follows

$$w_D = w_n^*(\bar{R}) = E_0 + w_0, \quad w_A = w_n^*(\bar{R}) = E_0 - w_0,$$

whereby these values are realized with the probabilities

$$p_D = 1/(1 + K), \quad p_A = K/(1 + K).$$

In accordance with results in remark [9], we get in this case, from the system of equations (5), (6) the equation for α

$$(E - E_0 - \bar{V})N_D/\alpha - w_0^2 - N_D w_0(1 - K)/((1 + K)\alpha) = 0. \qquad (7)$$

As it was stated above, in this case it is the question of the approximate solution of the problem. Therefore in order to simplify the analysis, we approximate the function $\bar{V}$

$$\bar{V} = mV_0/(1 - \alpha V_1 t) - (m - 1)V_0 \qquad (8)$$

where m, t are constants, which we choose so that when $K = 0$, the width

of the admixture band and the maximum $D(E)$ should be the same as in the work of $M - T$. For the sake of brevity let us denote $y = 1/(1 - \alpha V_1 t)$, $V_1 = K_{\kappa=0}$, $\Omega_0^{-1} = 1$ cm^3, $p = 32\pi N_D \alpha^{-3}\Omega_0^{-1}$, $A = t/m$, $E' = [E - E_0 + V_0(m - 1)]/(-V_0 m)$, $w = w_0/(V_0 m)$, where N_D is the total number of donors in 1 cm^3 of the sample and V_κ is given by relation (3). By applying these substances we get from (7) the equation for y:

$$y^3 + y^2[2E' - pA) - (1 - pA)] +$$
$$+ y[E'^2 - E'(2 - pA) - w^2 - wpA(1 - K)/(1 + K)] +$$
$$+ (w^2 - E'^2) = 0. \qquad (9)$$

From this equation it follows for the width of the admixture band at $K = 0$

$$\Delta E = (-V_0)4m\sqrt{pA}.$$

For the density of states we can write according to [9]

$$D(E) = (\pi N)^{-1} \text{Im}(\alpha^2\bar{V} + \alpha N)$$

and the reduced density of states $D'(E)$

$$D'(E) = -V_0 \alpha^{-3}\Omega_0^{-1}D(E) \times 10^2$$

can be expressed with the help of y by relation

$$D'(E') = (32\pi^2 t^2)^{-1} \text{Im}(1/y) \times 10^2 \qquad (10)$$

whereby we have omitted the other members, because their contribution is considerably smaller that of the remaining one. In case of Ge we consider $\alpha^{-1} = 65$ A°.

Let us choose the donors concentration $N_D = 2.9 \times 10^{17}$ cm^{-3}, which corresponds to $p = 8$; the values of t, m are $t = 0.268855$, $m = 2.3016$, $A = 0.116812$. $pA = 0.934497$. In Fig. 1, the dependence $D'(E')$ at different compensations of K is illustrated.

In the following we shall observe how far the conductivity depends on the compensation of K at $T = 0\,^\circ\text{K}$. The Fermi energy E_F at $T = 0\,^\circ\text{K}$ is specified by the equation $\int_{-\infty}^{E_F} dE\, D(E) = N_D(1 - K)/2$, where we have considered the spin degeneration and the fact that KN_D electrons are captured by the acceptors.

According to the work of M-K, M-T and others, for the conductivity averaged over a random decomposition of impurities at $T = 0\,^\circ\text{K}$, we can write

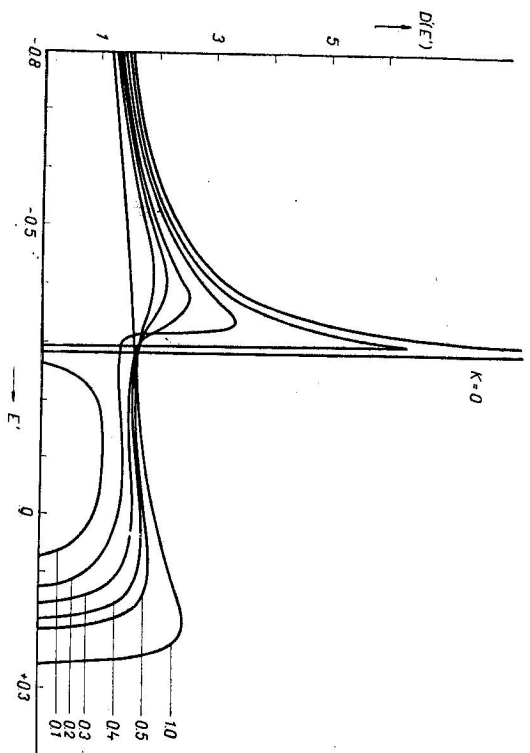$$\sigma = \sigma(E_F) = 2(\pi e^2/3h)\langle \Xi(E_F)\rangle,$$

Fig. 1. Density of states as a function of energy (both in reduced units) for different stages of compensation. Numerical values attached to individual curves denote the degree of the compensation K. Only the region of energies in which the compensation considerably influences the density course of states is illustrated.

where for [9], in accordance with M-T and M-K, (for a given concentration) we can use the approximation written according to [9] in the following form

$$\langle \Xi(E_F) \rangle = \pi^{-2} \sum_k |\partial V_k/\partial_k|^2 [\text{Im}(\alpha/(1 - \alpha V_k))]^2,$$

where α is the solution of equation (7) for $E = E_F$.

In order to determine the conductivity dependence σ from the compensation K, we have to determine $\langle \Xi(E_{FS}) \rangle$. By comparing (11) with the expression Ξ in the work of M-T, it follows that we can write

$$\langle \Xi(E_F) \rangle = 3a(4\pi^3)^{-1} \sum_{j=1}^{3} \text{Im} \left[\frac{t_j(3 + 7t_j^2)}{3(1 + t_j^2)} - \frac{2t_j^3(1 + t_j^2)^2}{\text{i Im}(X)} \right] \qquad (11)$$

where we proceeded from the summation accross $\boldsymbol{k}$ to the integration for $|\boldsymbol{k}| \in \langle 0, \infty)$ and V_k was approximated by the function $v(\boldsymbol{k}) = 32\pi V_0 a^3/ /(a^2 + k^2)^3$; t_j are the equation roots of $X = (1 + t_j^2)^3$ and $X = t^{-1}(1 - y^{-1})$, with the imaginary part of t_j positive and y the solution of equation (9) for $E = E_F$. The dependence of the function L on the compensation K is illustrated in Fig. 2, where L is given as $L = \sigma/(2e^2a/\hbar)$.
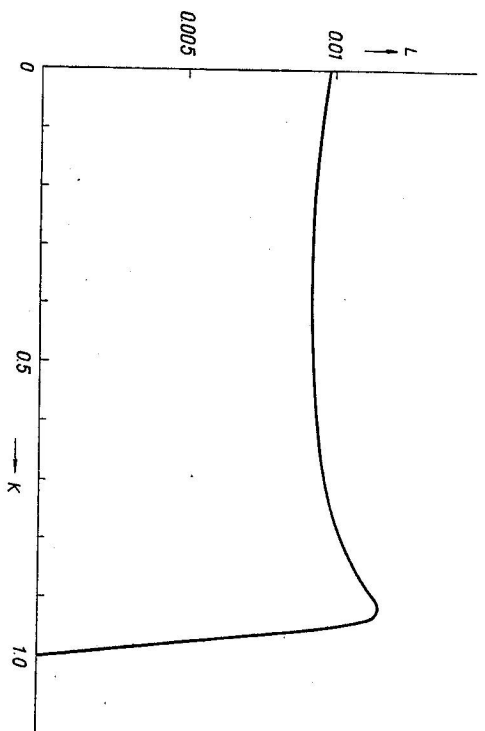
Fig. 2. Conductivity L (in reduced units) as a function of the compensation K for concentration of donors $N_D = 2.9 \times 10^{17}$ cm^{-3}.

We should like to add a few remarks in connection with the influence of the compensation on conductivity. As stated by Mott [5], for a degenerated electron gas in a random field at the temperature of $T = 0$ °K, there exists a minimum of metallic conductivity, if E_F lies on the "mobility edge" E_c. He support his theoretical estimate by the work of Allen and Adkins [2] and he uses their experimental results as a demonstration of the existence of a minimum of metallic conductivity. He refers to the fact that the donor concentration in Ge in the experiments in [2], is near the transition metal-nonmetal and probably on the side of metallic conductivity. As asserted by Mott [5] and Mott and Davis [6], a minimum metallic conductivity is realized when the compensation K acquires the value at which the resistance ϱ is becoming dependent on T. The results of work [2] are indicating that $\varrho \to \infty$ for $T \to 0$. A characteristic behaviour of $\ln \varrho$ as a function of $1/T^{1/4}$ strongly supports the idea, that at $T = 0$ °K a certain discontinuity exists in ϱ with a compensation growth, while the concentration of the donors is constant. The numerical value of the minimum metallic conductivity, according to Mott [5], could be obtained by comparing the results of Davis and Compton [7] with the results of Fritzsche and Lark-Horovitz [8], reproduced by Mott and Davis [6]. The results for σ_{min} give a value very close to 10 Ω^{-1} cm^{-1}, which belongs to the middle interdonor distance of approx. 100 A°. The concentration of donors in the examples cited in [8] was 2.5 × 10^{17} cm^{-3}.

IV. CONCLUSION

The course of the density of states in an impurity band for different compensations illustrated in Fig. 1 indicates that the method of including the influence of acceptors agrees with the theoretical assumptions. With a growing compensation, in agreement with the assumptions, the impurity band is extending and the maximum state density is decreasing. Results from Fig. 2 indicate that the proposed method of taking into account the compensation, allows to eliminate the difference between the theoretical calculation of the dependence of σ on the compensation in work [4] and the results which follow from the experiments quoted in work [2, 6, 7, 8]. From these works it follows that at $T \to 0$ °K, σ decreases with the growth of compensation, while in work [4], σ increases with the growth of compensation to a maximum for a certain K and then it decreases. From Fig. 2 it can be seen that in the first part of the plot σ is monotonously decreasing, which does agree with the experiment. In the second part of the plot, σ is no doubt growing, but this region is no essential, because for a great value of K, E_F is getting into the regions of localized states and thus $\sigma = 0$. The transition to $\sigma = 0$ occurs by a jump at a certain critical value of compensation.

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