Impurity conduction in n-type GaAs

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An investigation was made of the impurity (hopping) conduction in n-type gallium arsenide at liquid-helium temperatures as a function of the magnetic field intensity and impurity concentration. The experimental data on the dependences of ρ_3 on N_D and H, and of ε_3 on N_D were compared with the Shklovskii–Éfros theory. The experimental dependences of ρ_3 on N_D ($\alpha = 1.8$) and of ρ_3 on H ($t \approx 0.04$) were in good agreement with the theory of hopping conduction between shallow hydrogen-like levels.

At low temperatures, when phonons are no longer capable of transferring carriers to a conducting band, the conduction in a semiconductor is due to the motion of carriers directly between the impurity states. The overlap of the wave functions of the neighboring donors and the random potential of charged impurities essentially govern the magnitude of the impurity conductivity (resistivity) and the activated nature of its temperature dependence:[1,2]

$$\rho = \rho_3 \exp\left[\frac{\varepsilon_3}{kT}\right]. \quad (1)$$

The activation energy ε_3 is primarily governed by the Coulomb interaction between an acceptor and the nearest donor:[2,3]

$$\varepsilon_3 = C\frac{e^2 N_D^{1/3}}{\varkappa} f(K), \quad (2)$$

where $\varkappa$ is the permittivity; C is the numerical coefficient; $f(K)$ is a function which describes the dependence of ε_3 on the degree of compensation $K = N_A/N_D$; N_D and N_A are the donor and acceptor concentrations. The value of ρ_3 is an exponential function of the donor concentration since it is governed by the probability of a jump which is proportional to the overlap integral of the wave functions of impurities:

$$\rho_3 = \rho_0 \exp[f(N_D)]. \quad (3)$$

In the simplest variant of the theory of this phenomenon, the wave functions are assumed to be hydrogen-like, i.e., it is postulated that they decrease exponentially with the distance. Even in this case the coefficient C and the functions $f(K)$, $f(N_D)$ in Eqs. (2) and (3) depend very strongly on the selected impurity conduction based on the percolation model.[1)] A detailed analysis of the published experimental data, made by Éfros and Shklovskii, supports their theory. However, it must be stressed that practically all the hopping conduction investigations were carried out on Ge or Si. Although these crystals can be obtained in a homogeneous form and with known impurity concentrations, which are their undoubted advantages, the complex band structure of these materials gives rise to difficulties in quantitative comparisons of the experimental and theoretical results.

We investigated the impurity conduction of n-type GaAs because of its very simple parabolic and spherical isotropic conduction band. (A similar band is a feature of n-type InP and a detailed investigation of this material is in progress. For the sake of comparison, we shall include some results[5] for InP.) We can expect the structure of shallow donor centers in GaAs and InP to be close to the ideal hydrogen-like model and, therefore, quantitative comparisons of the experimental data on the hopping conduction between impurity states in these crystals with the theory of Shklovskii and Éfros can be made without adjustable parameters or additional assumptions.

EXPERIMENTAL RESULTS AND DISCUSSION

We selected the purest and most homogeneous samples of n-type GaAs, which were either undoped or contained S or Sn donors. The principal properties of the investigated samples are listed in Table 1. We determined the electrical resistivity ρ, magnetoresistance ρ_H/ρ, and Hall coefficient at liquid-helium temperatures in magnetic fields up to 30 kOe. The preparation method did not affect the results of measurements provided the initial high-temperature properties of the crystals were identical.

The Shklovskii–Éfros theory[3,4] can be compared with our experimental dependences of ρ_3 on N_D, ρ_3 on H, and ε_3 on N_D.

TABLE 1. Principal Properties of Investigated Samples

Sample No.	Impurity	n, cm^{-3} at 300°K	N_D, cm^{-3}	$K = \frac{N_A}{N_D}$
1	—	$6.4\cdot10^{14}$	$8.2\cdot10^{14}$	0.36
2	—	$2.5\cdot10^{15}$	$2.1\cdot10^{15}$	0.1
3	Sn	$1\cdot10^{15}$	$2.5\cdot10^{15}$	0.67
4	—	$4.9\cdot10^{15}$	$5.2\cdot10^{15}$	0.19
5	S	$3.5\cdot10^{15}$	$7.2\cdot10^{15}$	0.54
6	Sn	$2.3\cdot10^{16}$	$2.1\cdot10^{16}$	0.61

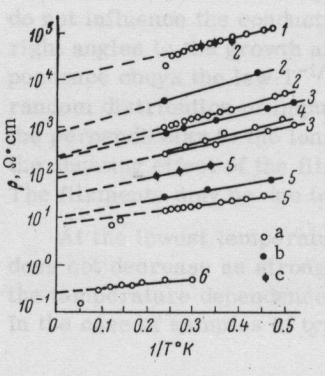

Fig. 1. Temperature dependences of the electrical resistivity in magnetic fields of various intensities H (kOe): a) 0; b) 15; c) 28.6. Numbers on curves correspond to sample Nos. in Table 1.

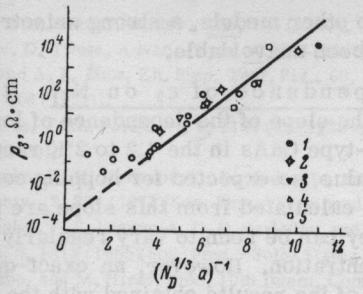

Fig. 2. Dependence of log ρ_3 on the average distance between impurities $(N_D^{1/3}a)^{-1}$. The experimental points: 1) our results; 2) results taken from ref. 7; 3) ref. 8; 4) ref. 9; 5) results for InP taken from ref. 5.

1. Dependence of ρ_3 on N_D. All the samples exhibit an exponential dependence of ρ on $1/T$ at $T < 5°K$ (Fig. 1). The value of ρ rises strongly when the donor concentration is reduced (by a factor of 10^4 when N_D is reduced from 10^{16} to 10^{15} cm^{-3}). The values of ρ_3 can be deduced from the experimental data by linear extrapolation of the low-temperature dependence to $1/T = 0$.

At low donor concentrations, when $(N_D^{1/3}a)^{-1} \gg 1$, the percolation method gives

$$f(N_D) = \frac{1.8}{N_D^{1/3}a}. \qquad (4)$$

The effective Bohr radius a for a simple hydrogen-like atom is

$$a = a_B \frac{\varkappa}{m^*}, \qquad (5)$$

where m^* is the effective mass of carriers and $a_B = 0.55$ Å is the Bohr radius.

The percolation method gives only the order of magnitude of ρ_0 and, therefore, a comparison with the theory is made first of all using the dependence of ρ_3 on $(N_D^{1/3}a)^{-1}$. Figure 2 shows our data for GaAs and InP, including those for the more heavily doped crystals taken from earlier investigations[6] and some of the published results[7,9] included for completeness. In the case of donor impurities in GaAs, we assumed that $a = 97$ Å, which corresponded to $m^* = 0.07m_0$ and $\varkappa = 12.5$; in the case of InP, we assumed that $a = 77$ Å, $m^* = 0.085m_0$, and $\varkappa = 14$.

The points for the samples with $\rho \leqslant 10^4$ Ω·cm are of greatest importance in the comparison with the theory because at high values of ρ the resistivity is strongly affected (reduced) by any random high-conductivity channel. In particular, in the case of the purest epitaxial crystals, the resistivity is always reduced by even a slight layer inhomogeneity because of the strong dependence of ρ on N_D.

On the other hand, if $(N_D^{1/3}a)^{-1} < 4$, the hopping conduction theory is no longer applicable (the Mott transition[2] takes place).

Bearing this point in mind, we can see that in the range of values of $(N_D^{1/3}a)^{-1}$ and ρ considered here (samples with 10^{15} cm$^{-3} \leqslant N_D \leqslant 10^{16}$ cm^{-3}) the experimental points are scattered somewhat (probably because of inaccurate values of N_D) but they do lie along a straight line with a slope of 1.8 (points 1 in Fig. 2), in accordance with Eq. (4). The extrapolation of the straight line to the ordinate gives about -3.5 for $\log \rho_0$. At low values of $(N_D^{1/3}a)^{-1}$, the experimental values lie above the extrapolated line. The location of the deviation from linearity is in approximate agreement with the location of the Mott transition, characterized by $\lambda_{cr} = (4/3\pi N_D)^{-1/3}a^{-1} = 0.62N_D^{-1/3}a^{-1} \approx 3$.

2. Dependence of ρ_0 on the magnetic field. Figure 3 shows the experimental results of an investigation of the dependence of the change in the resistivity ρ_H/ρ and $\rho_3(H)/\rho_3(0)$ on the magnetic field in the hopping conduction region of three samples of n-type GaAs. In the case of pure samples, an analysis of ρ_H/ρ is equivalent to an analysis of $\rho_3(H)/\rho_3(0)$ because the slope of the dependence $\rho(T)$ is practically unaffected by the application of a magnetic field (Fig. 1) and the ratio of the extrapolated values of ρ_3 is equal to the ratio ρ_H/ρ_0 at any temperature. Beginning from a certain value of H, we find that the resistivity rises exponentially with increasing magnetic field.[2)] The purer the sample, the greater is the increase in the resistivity. In fields $H > 20$ kOe the rise slows down for sample 2; the same slowing down is observed for the more heavily doped crystal 4 near 28 kOe.

The rise of the resistivity in a magnetic field is primarily due to the fact that the wave functions of donor impurities contract in a magnetic field so that their overlap becomes less. In the case of hydrogen-like functions, this results in an exponential rise of ρ.

In the case of lightly doped semiconductors, the application of a moderately strong field [$\lambda_0 > a/(N_D a^3)^{1/6}$, where $\lambda_0 = (\hbar c/eH)^{1/2}$ is the magnetic length] gives rise, according to Mikoshiba[10] and Shklovskii,[11] to the following expression for $\rho_3(H)$:

$$\rho_3(H) = \rho_3(0)\exp\left(\frac{ta}{N_D\lambda_0^5}\right), \qquad (6)$$

where t is a numerical coefficient.

It is clear from Eq. (6) that the quantity $\log[\rho_3(H)/\rho_3(0)]$ is proportional to H^2 and inversely proportional to N_D. The slope of the line in Fig. 3 drawn to through the points $\log[\rho_3(H)/\rho_3(0)]^{1/2} = f(H^2)$ yields the coefficient t which occurs in Eq. (6). The values of t found in this way (for $a = 97$ Å) are 0.046 and 0.036, respectively, for samples 2 and 5. These values are in good agreement with the theoretical prediction[3)] of $t = 0.04$. It should be noted that the

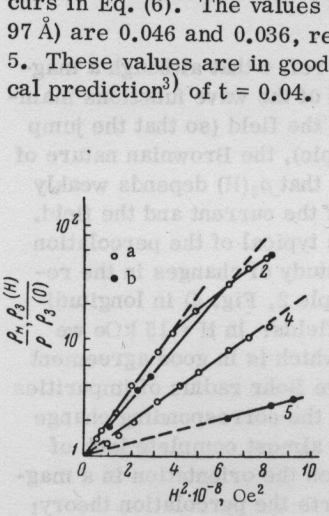

Fig. 3. Dependence of the magnetoresistance on the magnetic field at 2.6°K (sample 2) and 2.9°K (sample 4): a) ρ_H/ρ; b) $\rho_3(H)/\rho_3(0)$.

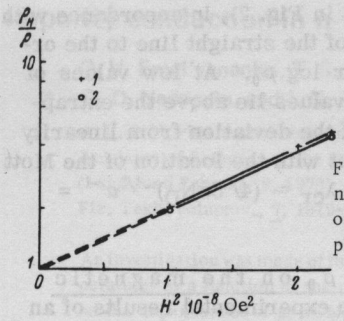

Fig. 4. Dependence of the longitudinal and transverse magnetoresistance on the magnetic field applied to sample 2 at 2.3°K: 1) $\rho_H^{\perp}/\rho$; 2) $\rho_H^{\parallel}/\rho$.

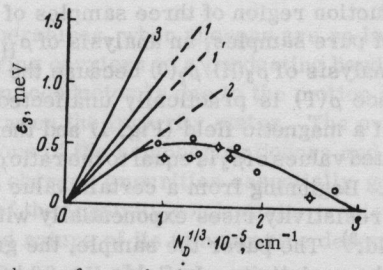

Fig. 5. Dependence of ε_3 on the donor concentration N_D. The designations of the experimental points are the same as in Fig. 2. Lines 1 and 1' represent the Shklovskii–Éfros theory for K = 0 and K = 0.2 (refs. 3 and 4); curve 2 is plotted for K = 0.4 (ref. 12); curve 3 represents the Miller–Abrahams[1] theory for K = 0.

value of t found experimentally[12] for p-type Ge differs by about 50% from the theoretical value; this discrepancy is not explained.

The reported slowing down of the rise ρ_H/ρ of sample 2 subjected to magnetic fields in excess of 20 kOe is due to the considerable change in the form of the wave functions at distances important in carrier jumps, which occurs when strong magnetic fields are applied. Consequently, changes in the percolation paths begin to play an important role and this results in a weaker dependence of the hopping resistivity on H (in the limit we approach the law $\rho_H/\rho \propto \exp H^{1/2}$). The magnetic field H_0 in which this transition should occur can be found theoretically[4] from the condition $\lambda_0 = (a/2)(N_D a^3)^{1/6}$. In our case, this gives $H_0 = 0.258 N_D^{1/3}$ and hence we find that $H_0 = 32.5$ kOe for sample 2; this is in good agreement with the experimental results if the finite width of the transition is taken into account.

Finally, it is reported in ref. 4 that although a magnetic field causes contraction of the wave functions mainly in a plane perpendicular to the field (so that the jump probability becomes anisotropic), the Brownian nature of the percolation paths ensures that $\rho_3(H)$ depends weakly on the relative orientations of the current and the field. This theoretical conclusion is typical of the percolation model and is supported by a study of changes in the resistivity of n-type GaAs (sample 2, Fig. 4) in longitudinal and transverse magnetic fields: In H = 15 kOe we find that $\rho^{\perp}(H)/\rho^{\parallel}(H) = 1.08$, which is in good agreement with the change in the effective Bohr radius of impurities $a(0)/a(H) = 1.1$, deduced from the corresponding change in the ionization energy. The almost complete lack of dependence of the resistivity on the orientation in a magnetic field convincingly supports the percolation theory; according to other models, a strong anisotropy of $\rho(H)$ would have been unavoidable.

3. Dependence of ε_3 on N_D. It is clear from Fig. 1 that the slope of the dependence of log ρ on $1/T$, obtained for n-type GaAs in the 4.2 to 2°K range, has a definite finite value, as expected for hopping conduction. The values of ε_3 calculated from this slope are plotted in Fig. 5, where they can be seen to vary regularly with the impurity concentration. However, an exact quantitative comparison of the results obtained with the theory is quite difficult.

First of all, the numerical values of the energy ε_3 can be calculated on the basis of the available theory only if the impurity compensation is very weak or very strong. Shklovskii and Éfros obtained the following expressions:

$$\varepsilon_3 = 0.99\frac{e^2 N_D^{1/3}}{\varkappa}(1 - 0.3K^{1/4}) \quad \text{for} \quad K \ll 0.2, \tag{6}$$

$$\varepsilon_3 = \nu\frac{e^2 N_D^{1/3}}{\varkappa}(1 - K)^{-1/3} \quad \text{for} \quad K \gg 0.5, \tag{7}$$

where ν must be found experimentally.

The theory suitable for the calculation of ε_3 is valid subject to an even more rigorous restriction as to impurity concentration than in the calculation[6] of ρ_3: this restriction is[4] $(N_D^{1/3}a)^{-1} > 9$, which is at the limit of the investigated range of impurity concentrations.

Since the degree of compensation of impurities in our samples ranged from ~ 0.1 to ~ 0.6, we compared our results with the theory using Eq. (7) with K = 0 and K = 0.2 (lines 1 and 1' for Fig. 5) and using Eq. (8) with ν = 0.6 (line 2), obtained experimentally[12] for p-type Ge with K = 0.4. Figure 5 includes also line 3 for $\varepsilon_3(N_D)$, in accordance with the Miller–Abrahams theory for K = 0. We can see that the extreme experimental points [$N_D < 10^{15}$ cm^{-3}, $(N_D^{1/3}a)^{-1} > 7$] approach the Shklovskii–Éfros curves and lie closest to line 2. The experimental values of ε_3 decrease with increasing donor concentration. This decrease of ε_3 can be explained qualitatively by the influence of the partial overlap of the impurity wave functions,[13] but rigorous calculations have not yet been made in this range of impurity concentrations. A complete overlap of the impurity states between themselves and the conduction band occurs at $N_D \gtrsim 10^{16}$ cm^{-3}: In this range the energy ε_3 tends to zero. This occurs in the region of the Mott transition, which has already been considered in the analysis of ρ_3.

We shall conclude by pointing out that, on the whole, the experimental results are in good agreement with modern theoretical ideas on hopping conduction.[1] Moreover, the donor impurities in GaAs can be described by the simplest hydrogen-like model.

The authors are grateful to B. I. Shklovskii for discussing the results of this investigation.

[1)] A critical analysis of the errors in the theoretical models and calculations of Miller and Abrahams[1] and of Mott and Twose[2] can be found, for example, in the review in ref. 4.

[2)] The magnetoresistance in weak magnetic fields (H < 2-5 kOe) is negative for all samples with $N_D > 10^{15}$ cm^{-3}.

[3)] B. I. Shklovskii kindly informs us that this more exact value is obtained if allowance is made for slight changes by the percolation.

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