

Impurity Conduction in Transmutation-Doped *p*-Type Germanium†

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The Hall coefficient and resistivity of germanium single crystals bombarded with slow neutrons were measured between 1.2 and 300°K. Slow neutron capture and subsequent nuclear transmutation produce majority impurities, gallium atoms, and compensating impurities, arsenic and selenium atoms. *p*-type samples with a gallium concentration ranging from 8×10^{14} to 5×10^{17} per cc with a fixed compensation ratio of 0.40 were thus prepared and the impurity conduction was studied as a function of the average distance between the majority impurities. The effective radius a of the acceptor ground-state wave function is 90.1 Å according to Miller's theory of impurity conduction, whereas $a = 40$ Å according to Twose's theory. The latter value agrees well with the effective radius of the Kohn-Schechter acceptor wave function. The activation energy of impurity conduction changes slowly with impurity concentration from 3.5×10^{-4} to 5.9×10^{-4} eV and agrees well with the predictions of Miller's theory for gallium concentration below 5×10^{15} per cc. Measurements on samples which contain different dislocation densities but identical impurity concentrations show that up to 10^4 dislocations per cm^2 do not affect impurity conduction.

I. INTRODUCTION

IMPURITY conduction has been observed in many semiconductors^{1,2} at low temperatures. It has been investigated in considerable detail both experimentally³⁻⁵ and theoretically.⁶⁻¹¹

One of the most striking properties of impurity conduction, which distinguishes it from ordinary semiconductor conduction, is the fact that it increases much more rapidly than linearly with impurity concentration. This strong dependence on concentration led Hung¹ to suggest that the impurity conduction process in germanium below about 5°K, is due to a charge exchange between neighboring impurity sites. This exchange results from a small but finite overlap of the localized wave functions of the individual impurity centers. Because it

is relatively small, impurity conduction becomes noticeable only at low temperatures where a negligibly small number of carriers are excited into their respective conduction band. The extensive experimental work on impurity conduction published so far has helped very much in elucidating the qualitative nature of this conduction process. If one tries, however, to extract some quantitative results from these earlier data one meets great difficulties, since pertinent quantities like the activation energy and the absolute magnitude of impurity conduction scatter over too large a range when one compares apparently equivalent samples of different investigators.

The reason for this is most likely the fact that the chemical composition of the material is not known accurately enough, particularly the compensation ratio K , the ratio of minority to majority impurity concentrations, which strongly affects the magnitude and the temperature dependence of impurity conduction. The influence of the presence of compensating impurities has been demonstrated experimentally^{4,5,12,13} and discussed theoretically^{7,8} by several authors. It arises from the fact that the only charge transitions which can yield a net transport of charge at low impurity concentrations are those from occupied to vacant majority centers. The concentration of the latter is equal to the concentration of compensating minority impurities.

In the present work we want to establish the dependence of impurity conduction on the separation of the interacting majority impurities. Although experimental evidence and theoretical studies indicate an exponential dependence of impurity conduction on impurity separation in the range of low impurity concen-

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¹ C. S. Hung, Phys. Rev. **79**, 727 (1950).

² SiC: G. Busch and H. Labhart, Helv. Phys. Acta **19**, 463 (1946); Ge: C. S. Hung and J. R. Gliessman, Phys. Rev. **79**, 726 (1950); **96**, 1226 (1954); CdS: F. A. Kröger, H. J. Vink, and J. Vogler, Physica **20**, 1095 (1954); Si: F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954), R. O. Carlson, Phys. Rev. **100**, 1075 (1955); *p*-InSb: H. Fritzsche and K. Lark-Horovitz, Phys. Rev. **99**, 400 (1955); *n*-InSb: R. J. Sladek, J. Phys. Chem. Solids **5**, 157 (1958); Te: T. Fukuroi, S. Tanuma, and Y. Mutō, Sci. Repts. Research Inst. Tohoku Univ. **A6**, 18 (1954).

³ H. Fritzsche, Phys. Rev. **99**, 406 (1955).

⁴ S. H. Koenig and G. R. Gunther-Mohr, J. Phys. Chem. Solids **2**, 268 (1957).

⁵ H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).

⁶ C. Erginsoy, Phys. Rev. **80**, 1104 (1950), **88**, 893 (1952); X. Baltensperger, Phil. Mag. **44**, 1355 (1953); P. Aigrain, Physica **20**, 978 (1954).

⁷ N. F. Mott, Can. J. Phys. **34**, 1356 (1956).

⁸ E. M. Conwell, Phys. Rev. **103**, 51 (1956).

⁹ T. Kasuya and S. Koide, J. Phys. Soc. Japan **13**, 1287 (1958).

¹⁰ W. D. Twose, Ph.D. thesis, Cambridge University, 1959 (unpublished).

¹¹ A. H. Miller, Ph.D. thesis, Rutgers University, 1960 (unpublished).

¹² H. Fritzsche and K. Lark-Horovitz, Phys. Rev. **113**, 999 (1959).

¹³ J. S. Blakemore, Phil. Mag. **4**, 560 (1959).

trations, the precise relationship has not been previously determined experimentally. Because of the reasons mentioned above, the compensation ratio K has to be exactly the same for all samples in order to determine the dependence of impurity conduction on impurity separation. Such control, however, is practically impossible to realize in crystals grown from melts and doped with the desired impurities. In the present investigation, this difficulty was avoided by introducing donor and acceptor impurities into pure germanium single crystals by slow neutron bombardment.¹⁴ The relative concentrations of the different kinds of impurities which are produced after the transmutation of those nuclei which have captured a slow neutron is completed are determined by the abundances and capture cross sections of the various germanium isotopes. The ratio of minority to majority impurities is, therefore, the same for all bombarded specimens. The absolute magnitudes of the impurity concentrations, however, can be varied over a wide range since they depend on the neutron flux and the exposure times. These transmutation-doped semiconductors contain Ga as majority impurities. The compensation ratio is $K=0.40$. The compensating impurities are As and Se.

We have measured the Hall coefficient and the resistivity of transmutation-doped germanium between 300 and 1.2°K. The specimens contain between 8×10^{14} and 5×10^{17} Ga atoms per cc and a correspondingly smaller concentration of compensating As and Se atoms. The dependence of the resistivity of impurity conduction on impurity separation has been determined and the results compared with the theories of Twose¹⁰ and of Miller.¹¹

II. EXPERIMENTAL DETAILS

Pure single crystals of germanium having resistivities at room temperature larger than 30 ohm-cm were used for the neutron irradiation. A number of samples were exposed¹⁵ to a neutron flux of 1.3×10^{13} thermal neutrons/cm² sec and about 2.9×10^{12} fast neutrons/cm² sec in the reactor of the Oak Ridge National Laboratory. Others were irradiated in the CP-5 reactor of the Argonne National Laboratory in which the ratio of thermal to fast neutrons is much larger, namely, 100:1. In the latter case, the flux was 10^{12} thermal neutrons/cm² sec.

The reactions following neutron capture by the various Ge isotopes have first been discussed by Cleland et al.¹⁴ Table I lists the three nuclear reactions, as given by Schweinler,¹⁶ which result in electrically active impurities. This method of introducing impurities into germanium avoids many difficulties arising from a non-uniform distribution of the impurities since the attenua-

TABLE I. Slow neutron reactions yielding electrically active impurities in germanium.

| Percentage of neutrons captured | Reaction |
|---------------------------------|---|
| 30.4% | $\text{Ge}^{70}(n\gamma)\text{Ge}^{71} \xrightarrow[\text{K}]{12d} \text{Ga}^{71}$ |
| 9.8% | $\text{Ge}^{74}(n\gamma)\text{Ge}^{75} \xrightarrow[\beta]{82m} \text{As}^{75}$ |
| 1.2% | $\text{Ge}^{76}(n\gamma)\text{Ge}^{77} \xrightarrow[\beta]{12h} \text{As}^{77} \xrightarrow[\beta]{38.8h} \text{Se}^{77}$ |

tion length of the thermal neutron flux due to the capture processes is several centimeters, which is much larger than the dimensions of the specimens used.

Since each Se donor will be doubly charged and hence can compensate two acceptors, it is more reasonable to define the compensation ratio as the ratio of charged majority impurities to the total number of majority impurities at zero absolute temperature. Using this definition the compensation ratio is $K=0.40$ for transmutation-doped germanium, as can be seen from Table I. We believe that this value of K is more accurate than the value $K=0.33$ used earlier which was based on older capture cross-section data and which neglected the presence of Se.

About one year after neutron irradiation, i.e., after many half-lives of the longer living Ge^{71} , the specimens were annealed for 48 hours in a vacuum at various temperatures between 350 and 460°C to assure complete healing of the radiation damage. This damage is caused by the high-energy particles present in the thermal neutron beam and by the recoil energy following neutron capture.¹⁶ The radiation damage was about ten times larger for the Oak Ridge samples than for the Argonne samples because of the larger fast particle flux present in the Oak Ridge reactor. The fact that both kinds of samples, some with a large amount and others with a much smaller amount of initial radiation damage, show the same electrical behavior after annealing indicates that the annealing process effectively healed out all radiation damage.

In order to test the influence of dislocations on impurity conduction, two pure samples containing 5×10^3 and 10^4 dislocations per cm² were irradiated with the same amount of slow neutrons. No difference in the electrical behavior of the two samples could be detected. We conclude from this that dislocation densities up to 10^4 /cm² do not affect impurity conduction.

The cryostat and the electrical measuring system are similar to those described earlier.¹⁷ To avoid errors due to the hysteresis of the magnet, the sample was rotated for the Hall measurements in a constant field of 7000 gauss. Temperatures below the λ point were obtained

¹⁴ J. W. Cleland, K. Lark-Horovitz, and J. C. Pigg, Phys. Rev. **78**, 814 (1950).

¹⁵ We are very grateful to J. W. Cleland for irradiating some of our specimens in the Oak Ridge National Laboratory reactor.

¹⁶ H. C. Schweinler, J. Appl. Phys. **30**, 1125 (1959).

¹⁷ H. Fritzsche and K. Lark-Horovitz, Physica **20**, 834 (1954).

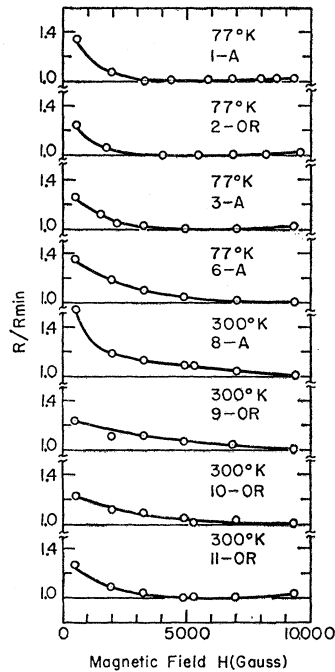


FIG. 1. Relative change of the Hall coefficient R with magnetic field at 77°K and 300°K for some typical cases. The values of R_{\min} are those listed in Table II.

from the vapor pressure of the liquid helium. Temperatures above the λ point were measured with a 0.10 watt carbon resistor which was calibrated against a vapor pressure bulb. This avoids inaccuracies caused by the temperature drop¹⁸ at the surface of the helium bath between the λ point and the boiling point of He. Constant temperatures above 4°K were achieved by using the He desorption method.¹⁹

1. Concentrations of Impurities

For the compensation ratio $K = (N_{As} + 2N_{Se})/N_{Ga}$ we used the value $K = 0.40$ which was calculated from the relative abundances and capture cross sections of the Ge isotopes. Knowing K , one can obtain the concentra-

TABLE II. R and ρ at 300°K and 77°K.

| Sample | 300°K | | 77°K | |
|-------------------|------------------|---|------------------|---|
| | ρ ohm-cm | R cm ³ coul ⁻¹ | ρ ohm-cm | R cm ³ coul ⁻¹ |
| 1-A ^a | 6.87 | 1.84×10^4 | 0.574 | 1.39×10^4 |
| 2-OR ^b | 3.84 | 9.14×10^3 | 0.379 | 7.64×10^3 |
| 3-A | 3.51 | 9.060×10^3 | 0.333 | 6.922×10^3 |
| 4-A | 1.48 | 3.50×10^3 | 0.210 | 2.92×10^3 |
| 5-OR | 1.12 | 2.44×10^3 | 0.177 | 2.13×10^3 |
| 6-A | 0.710 | 1.53×10^3 | 0.145 | 1.44×10^3 |
| 7-OR | 0.603 | 1.19×10^3 | 0.137 | 1.156×10^3 |
| 8-A | 0.259 | 4.30×10^2 | 0.093 | 5.37×10^2 |
| 9-OR | 0.201 | 2.94×10^2 | 0.092 | 3.91×10^2 |
| 10-OR | 0.063 | 69.0 | 0.058 | 1.04×10^2 |
| 11-OR | 0.030 | 20.9 | 0.034 | 24.4 |

^a A refers to samples bombarded at Argonne National Labs.

^b OR refers to samples bombarded at Oak Ridge National Lab.

¹⁸ F. E. Hoare and J. E. Zimmerman, Rev. Sci. Instr. **39**, 184 (1959).

¹⁹ A. C. Rose-Innes and R. F. Broom, J. Sci. Instr. **33**, 31 (1956).

tions of the different impurities from the Hall coefficient, $R = (\mu_H/\mu_D)1/en$, where at exhaustion $n = N_{Ga} - (N_{As} + 2N_{Se})$. In the case of p -type samples an accurate determination of carrier concentration n from the Hall coefficient is complicated because of the presence of a small concentration of light holes.²⁰ The ratio of Hall to drift mobilities μ_H/μ_D depends in that case quite strongly on the field strength and in general it is anisotropic. The low field and the high field limits of R , R_0 and R_∞ , respectively, are isotropic and easiest to interpret. The low field limit R_0 , however, is difficult to obtain because of the low accuracy of the measurements at very small fields. Moreover, the interpretation of R_0 depends on theoretical values of μ_H/μ_D which are of the order of 2 and quite uncertain particularly if, as in our case, a considerable contribution of ionized impurity scattering is present. We have measured R of our samples as a function of magnetic field strength H . The results are shown in Fig. 1 for some typical cases. At the highest fields available R is almost independent of H . This, however, does not necessarily indicate that the high

TABLE III. Gallium concentrations and resistivity parameters^a of transmutation-doped germanium specimens.

| Sample | N_A cm ⁻³ | ϵ_3 10 ⁻⁴ ev | C ohm-cm |
|--------|---------------------------|-------------------------------------|-------------------|
| 1-A | 7.47×10^{14} | 3.23 | 1.9×10^8 |
| 2-OR | 1.36×10^{15} | 5.2 | 1.5×10^6 |
| 3-A | 1.50×10^{15} | 5.2 | 1.0×10^6 |
| 4-A | 3.56×10^{15} | 5.9 | 6.8×10^3 |
| 5-OR | 4.87×10^{15} | 5.75 | 1.8×10^3 |
| 6-A | 7.20×10^{15} | 5.4 | 5.9×10^2 |
| 7-OR | 9.00×10^{15} | 5.0 | 2.3×10^2 |
| 8-A | 2.42×10^{16} | 4.2 | 19 |
| 9-OR | 3.54×10^{16} | 4.7 | 4.9 |
| 10-OR | 1.51×10^{17} | ... | 0.16 |
| 11-OR | 4.97×10^{17} | ... | 0.035 |

^a See Eq. (1) of text.

field limit R_∞ is approached, for which $\mu_H/\mu_D = 1$. Theoretical calculations by Beer *et al.*²¹ of μ_H/μ_D as a function of H for various mixtures of lattice and impurity scattering have shown that R reaches a plateau or even shows a slight maximum at large values of H before R_∞ is reached. A comparison of the R versus H curves of Fig. 1 with the theoretical results suggests that the measured Hall coefficients at large fields probably are still as much as 10% higher than R_∞ .

Table II lists the zero field resistivity ρ and the Hall coefficient measured at high fields for our samples. The acceptor concentrations N_A listed in Table III were obtained from these high field Hall coefficients using $K = 0.40$ and $\mu_H/\mu_D = 1$. Because of the reasons mentioned above, the correct values of N_A may lie up to 10% higher. At the present time we are not able to calculate the exact correction factor. The remaining un-

²⁰ R. K. Willardson, T. C. Harman, and A. C. Beer, Phys. Rev. **96**, 1512 (1954).

²¹ A. C. Beer and R. K. Willardson, Phys. Rev. **110**, 1286 (1958).

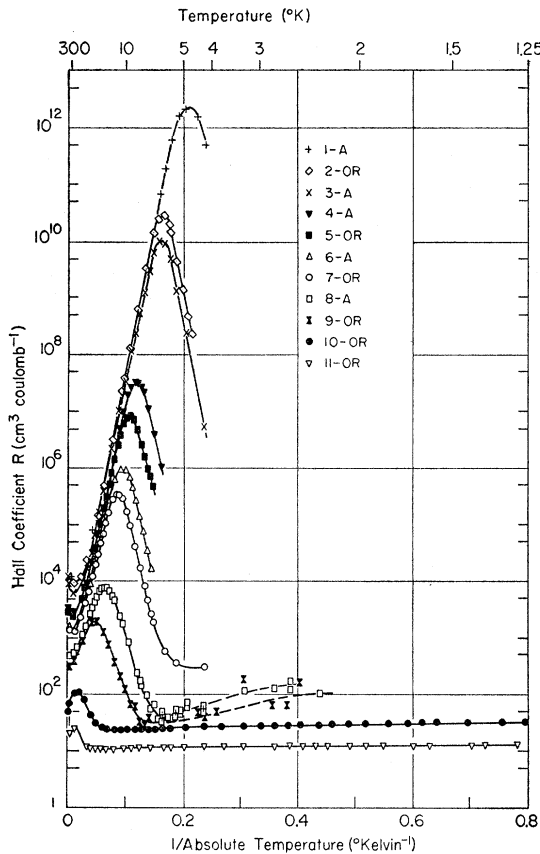


FIG. 2. Hall coefficient of transmutation-doped germanium (p type) as a function of $1/T$.

certainty in N_A , however, does not influence the conclusions drawn from our final results.

III. RESULTS

The measurements of the Hall coefficient are shown in Fig. 2. For majority impurity concentrations $N_A < 2 \times 10^{16}/\text{cc}$ the Hall curves show a single maximum which is characteristic of the presence of the two competing conduction processes, impurity conduction at low temperatures and valence band conduction at higher temperatures. As shown previously,¹⁷ the Hall maximum occurs at the temperature at which the two conduction processes yield the same conductivity. The rapidly decreasing Hall coefficient at temperatures below the Hall maximum can be attributed to the decreasing contribution of valence band conduction to the total current.

Only the two lowest Hall curves could be extended to the lowest temperatures. The others terminate because the present experimental setup does not enable us to detect a Hall effect when the effective Hall mobility R/ρ drops below about $3 \text{ cm}^2/\text{volt sec}$.

At low temperatures the samples 10-OR and 11-OR have a temperature independent R and ρ which is a behavior characteristic of the metallic type of conduc-

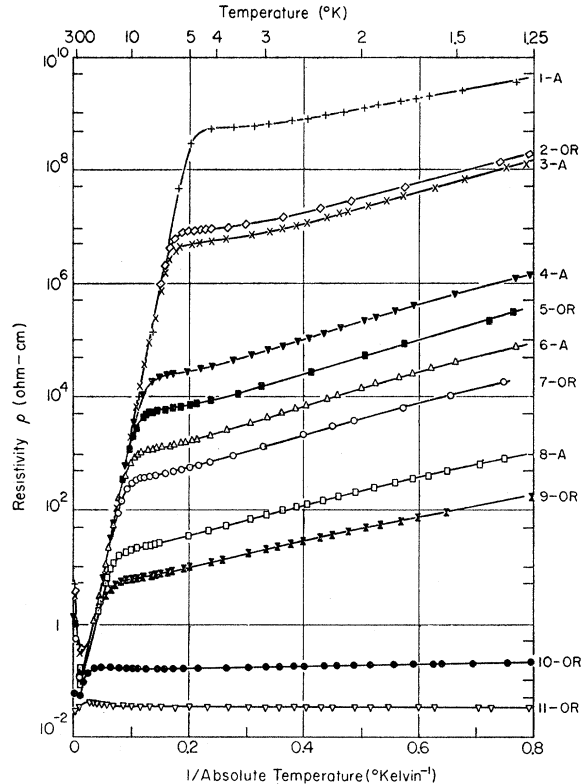


FIG. 3. Resistivity of transmutation-doped germanium (p type) as a function of $1/T$.

tion of the high concentration range.^{5,7,12} The Hall coefficients of samples 8-A and 9-OR reach a minimum value near 6°K which is 8 times smaller than the Hall coefficient at exhaustion ($77^\circ\text{--}300^\circ\text{K}$). The Hall coefficient of sample 7-OR near 5°K is about 4 times smaller than the value at exhaustion. It remains uncertain whether the Hall coefficient of 7-OR has reached a minimum value near 5°K since the Hall curve terminates at that temperature. It is doubtful whether the Hall coefficients below 6°K of these last three samples can be attributed to impurity conduction at sufficiently low concentrations so that the localized orbital approximation should be valid. These samples lie at the borderline of the so-called intermediate concentration range⁵ ($1 \times 10^{16} < N < 8 \times 10^{16}$) for which the simpler model of impurity conduction does not seem to be valid. This intermediate concentration range and the transition to metallic type of conduction for transmutation-doped germanium will be the subject of a separate study.

Figure 3 shows the resistivity curves of our samples. Most striking seems the fact that the activation energy of impurity conduction, previously³ called ϵ_3 , is almost independent of impurity concentration. Here we disregard the two samples showing the metallic type of conduction. The activation energies ϵ_3 , as measured from the slopes of the resistivity curves at the lowest temperatures, are listed in Table III and plotted against

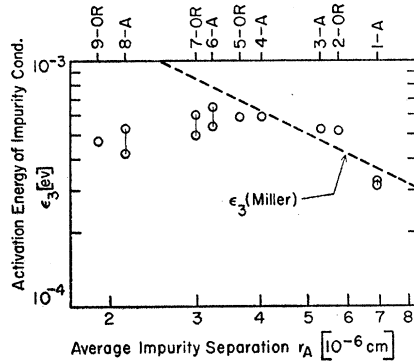


FIG. 4. Activation energy ϵ_3 of impurity conduction [as defined by Eq. (1) of text] as a function of the average separation of majority impurities. The dashed curve represents Miller's calculated values according to Eq. (10) of text.

the average impurity separation r_A in Fig. 4. This curve shows a slight maximum. The apparent drop of ϵ_3 at large r_A , however, is based on only one sample and should be considered tentative until this behavior has been confirmed by further measurements. Some resistivity curves of Fig. 3 are not completely straight lines at low temperatures. This deviation from linearity causes some uncertainty in the determination of ϵ_3 , which is indicated by vertical bars in Fig. 4. The resistivity curves for samples with $N_A < 2 \times 10^{16}/\text{cc}$ seem to reach a plateau in the impurity conduction range just before they drop sharply at higher temperatures where the normal valence band conduction predominates. Such a plateau has been observed before in lightly compensated n -Ge⁵ and p -Ge.^{3,13} In the impurity conduction region at the lowest temperatures

$$\rho = C \exp(\epsilon_3/kT), \quad (1)$$

where ρ is the resistivity and C a temperature independent factor. The dependence of C on impurity separation is exhibited in Table III.

IV. DISCUSSION

In this section, the experimentally observed separation dependence of C and the observed values of the activation energy ϵ_3 will be compared with the theories of impurity conduction worked out by Miller¹¹ and by Twose,¹⁰ who have improved and extended the earlier work of Kasuya and Koide.⁹

2. Comparison with the theory of A.H. Miller

Miller calculated an expression for impurity conduction assuming that the "resonance" energy of a neighboring pair of impurities is much smaller than their difference in potential energy arising from the variation in local fields produced by nearby ionized acceptors and donors. This condition holds at low impurity concentrations ($< 5 \times 10^{15}/\text{cc}$ in germanium) where the overlap of neighboring wave functions is small. A charge transfer is possible in this case only if it is accompanied by the

emission or absorption of a phonon. Miller computed the transition rate between occupied and vacant impurity sites from the matrix element of the electron-phonon interaction potential. He then computed the Fermi energy of the steady state charge distribution. The problem of calculating the net current in the presence of an external electric field was transformed to that of solving an equivalent resistance network. The randomness of the distribution of impurities has been taken into account. Miller's final expression for the resistivity of impurity conduction of p -Ge as a function of the average acceptor separation r_A and of temperature is

$$\rho = \text{const} r_A^{-11/4} \exp[1.09(r_A/a)^3] \exp(\epsilon/kT), \quad (2)$$

where

$$r_A = (3/4\pi N_A)^{1/3}.$$

The parameter a is analogous to the Bohr radius of the hydrogen ground-state wave function and determines the exponential decay of the acceptor wave functions at large distances.

In order to determine the parameter a of Eq. (2) from the experimental results, we plotted $\log C r_A^{11/4}$ versus r_A^3 in Fig. 5. The points, belonging to samples which contain less than 7×10^{15} Ga/cc lie on a straight line and thus seem to follow an expression of the form (2). The limiting concentration $7 \times 10^{15}/\text{cc}$ agrees well with the critical concentration $5 \times 10^{15}/\text{cc}$ given by Miller, above which his calculations cease to be applicable. From the slope of the straight line of Fig. 5 one obtains $a = 90.1$ Å. This value is more than a factor of

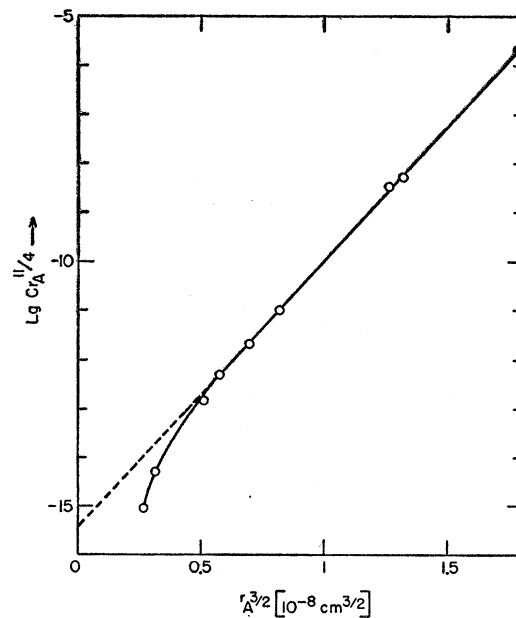


FIG. 5. Plot of the experimentally obtained values for $\log C r_A^{11/4}$ versus r_A^3 . From the slope of the straight line the parameter a of Miller's theory can be determined according to Eqs. (1) and (2) of text.

two larger than the value $a \approx 40$ Å expected from the Kohn-Schechter wave functions²² or the value $a = 41.4$ Å which is obtained by adjusting the radius of hydrogenic 1s-wave functions to yield the observed ionization energy of Ga acceptors in germanium.

Because of the complicated form of the Kohn-Schechter acceptor wave functions used for the calculation of Eq. (2), Miller's result for *p*-Ge is less certain than his result for *n*-Ge. This uncertainty, however, concerns only the pre-exponential factor $r_A^{-11/4}$ which does not greatly affect the value of a . Miller's resistivity expression for *n*-Ge contains the same exponential factor as that of Eq. (2) with r_A replaced by the average donor separation r_D . The value of a obtained from the experimental results depends sensitively on the form of the exponent of Eq. (2). The particular form of this exponent results from the statistical average over paths of easiest flow of current which extend through the length of the crystal. Although Miller devoted great care in constructing these current paths through the three-dimensional random array of impurity atoms, this calculation is by necessity only an approximate solution of this intricate problem.

The fact that the comparison with Miller's result yield a value of a which is too large by a factor of two may indicate that his averaging procedure overestimates the contribution to the total resistivity of impurities separated by more than the average distance.

Another explanation for the large value of a was proposed by Abrahams.²³ He suggested that it may possibly arise from higher spherical harmonics in the Kohn-Schechter acceptor function which will not be important for the binding energy but may extend far out compared to the parts considered by Kohn and Schechter.²²

Miller investigated the effect of a magnetic field on impurity conduction. According to his theory no Hall effect should exist in the low concentration range. The finite Hall coefficients below 6°K of samples 7-OR, 8-A, and 9-OR do not disagree with Miller's prediction since the acceptor concentrations of these samples are larger than the limiting concentration of about 5×10^{15} per cc given by Miller. If one assumes that the concentration of carriers contributing to impurity conduction is equal (or smaller) than the carrier concentration at exhaustion, then one obtains ratios of Hall to drift mobilities for these three samples in the impurity conduction range which are between $\frac{1}{4}$ and $\frac{1}{8}$ (or smaller). These unusually small Hall to drift mobility ratios in the transition range may be an indication that these mobility ratios become much smaller or even vanishingly small in the low concentration range in accordance with Miller's theory.

3. Comparison with the theory of Twose

Twose¹⁰ calculated the conductivity of impurity conduction for low impurity concentrations in the following steps. (i) Localized impurity wave functions as modified by the lattice vibrations were calculated in the Born-Oppenheimer approximation. (ii) The field dependent velocity of an electron between an occupied and a vacant center was calculated as a function of the center separation and the energy difference between the two centers using a density matrix similar to that of Greenwood²⁴ and Kohn and Luttinger.²⁵ (iii) A "two center" conductivity was then obtained from the term in the velocity expression which is linear in electric field strength. (iv) Finally, the "two center" conductivities were averaged over the random distribution of impurity centers. Two solutions of this problem were tried. The first, a very rough and approximate solution, is to substitute for the center separation in the "two center" conductivity the average separation of the majority impurities and to make this total conductivity proportional to the total number of occupied-vacant center pairs. The total resistivity has then the form

$$\rho = \frac{Mv^2(k\Theta)^3}{3\pi e^2 \hbar C_1^2} \frac{1}{|\langle i | \mathbf{v} | j \rangle|^2 (N_{\text{maj}} N_{\text{min}})^{\frac{1}{2}}}, \quad (3)$$

where M = mass of the Ge-atom, v = sound velocity, Θ = Debye temperature, C_1 = the Bardeen-Shockley deformation potential²⁶ and N_{maj} and N_{min} denote the majority and minority concentrations, respectively. The main part of the separation dependence of ρ is contained in $|\langle i | \mathbf{v} | j \rangle|^2$, the square of the velocity matrix element, in which i and j are the ground-state wave functions of two neighboring impurities. In this approximation the velocity matrix element is evaluated for the average separation.

Because of the complicated form of the ground-state acceptor wave functions the correct velocity matrix element could not be calculated. Since we are at present interested only in the dependence of ρ on r_A , we approximated the Kohn-Schechter envelope functions of the acceptor ground state by the spherically symmetric function,

$$F(r) = A_1 \exp(-r/a_1) + A_2 r^2 \exp(-r/a_2), \quad (4)$$

where the parameters $a_1 = 43.3$ Å and $a_2 = 33.8$ Å are the same as those of the Kohn-Schechter functions. In Fig. 6 the two theoretical curves *I* and *II* represent the temperature independent part of the resistivity of Eq. (3). The curve *I* was obtained by calculating the velocity matrix element setting $A_2 = 0$, i.e., using only the *s*-wave term of $F(r)$; curve *II* was obtained by setting $A_1 = 0$, i.e., using only the *d*-wave term of $F(r)$. If one

²² W. Kohn and D. Schechter, Phys. Rev. **99**, 1903 (1955).

²³ Private communication with Dr. E. Abrahams.

²⁴ D. A. Greenwood, Proc. Phys. Soc. (London) **71**, 585 (1958).

²⁵ J. M. Luttinger and W. Kohn, Phys. Rev. **108**, 590 (1957); **109**, 1892 (1958).

²⁶ J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

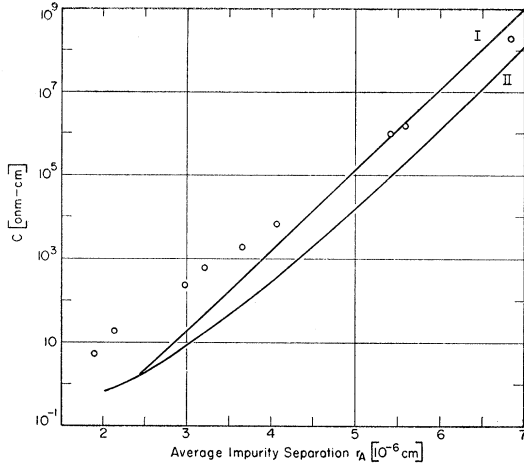


FIG. 6. Dependence of the temperature independent factor C [see Eq. (1) of text] on the average impurity separation. The circles represent the experimental data. Curves *I* and *II* were calculated from Twose's theory assuming all majority impurities separated by their average separation. For curve *I* only the s -wave part, for curve *II* only the d -wave part of the acceptor wave function was used in the calculation.

uses the complete envelope function $F(r)$ one would obtain a weighted average of the curves *I* and *II* plus terms which mix the s wave of one center with the d wave of the other center. Such a curve would lie between curves *I* and *II* but closer to curve *II*, because curve *II* yields a lower resistivity in the range of r_A considered here.

We cannot make an absolute magnitude comparison between curves *I* and *II* and the experimental points in Fig. 6 because we used $F(r)$ in place of the correct envelope function. The separation dependence, however, should not be altered by this approximation. Adjusting a_1 and a_2 for the best fit of the slopes of *I* and *II*, respectively, with the experimental points (see Fig. 7) we obtained $a_1 = 37$ Å and $a_2 = 55$ Å. These values should be compared with the values obtained by Kohn and Schechter.

Another method of averaging the two center conductivities over the random impurity distribution has been worked out by Twose, following a suggestion by Pippard. It is briefly the following. Let a given center pair, separated by a distance R , be surrounded by a sphere of radius R . The conductivity of this sphere is assumed to be uniform and equal to $\sigma(R)$, the two center conductivity for the separation R . Let this sphere be imbedded in a medium which has the average conductivity $\bar{\sigma}$ of the crystal as a whole. If a field E is applied to the crystal, the field inside the sphere is

$$\mathbf{E}(R) = \frac{3\bar{\sigma}}{2\bar{\sigma} + \sigma(R)} \mathbf{E}. \quad (5)$$

The current density inside the sphere is $E(R)\sigma(R)$. If the probability of finding a sphere with a radius between

R and $R+dR$ is $P(R)dR$, then the average current density will be

$$\mathbf{j}_{av} = \bar{\sigma} \mathbf{E} = \int_0^\infty P(R) \frac{3\bar{\sigma}\sigma(R)}{2\bar{\sigma} + \sigma(R)} \mathbf{E} dR. \quad (6)$$

For a random impurity distribution the probability function $P(R)$ is

$$P(R) = 4\pi N_{maj} R^2 \exp(-\frac{4}{3}\pi N_{maj} R^3). \quad (7)$$

Twose solved the integral equation (5) for $\bar{\sigma}$ by means of a computer using hydrogenic s -wave functions for the computation of the velocity matrix element in Eq. (3). The dependence of the average resistivity $\bar{\rho}$, obtained in this way, on the average separation of majority impurities $r_{maj} = (3/4\pi)^{1/3} N_{maj}^{-1/3}$ can be expressed as

$$\bar{\rho} = \text{const} \exp(1.46 r_{maj}/a). \quad (8)$$

A comparison of our experimental results with Eq. (8) implies that the acceptor wavefunction is approximated by a hydrogenic s function.

In Fig. 7 curve *III* shows an attempt to draw a straight line through the experimental points representing the purer samples, for which the Twose calculation should be applicable. From the slope of the straight line *III* and Eq. (8) the value $a = 40$ Å was obtained for the effective radius of the ground-state orbital. This value should be compared with $a = 41.1$ Å, which is obtained by adjusting the ground-state orbital radius to yield the experimentally observed ionization energy of gal-

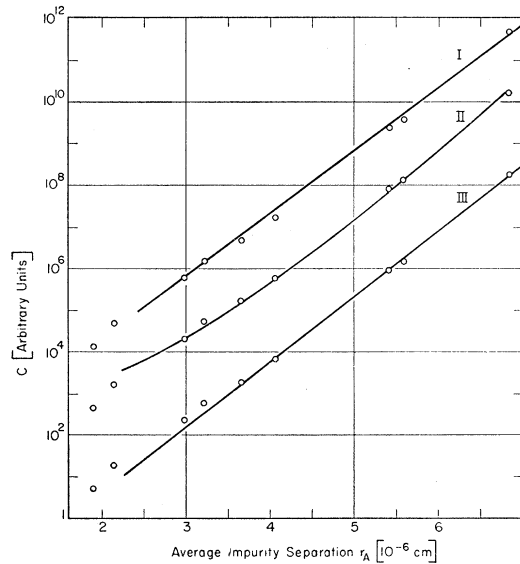


FIG. 7. The best fit of the experimental data with curves *I*, *II*, and *III*, obtained by adjusting the parameter a which determines the exponential decrease of the acceptor wave function at large distances. The vertical scale is shifted so that the experimental points fall on the theoretical curves. Curves *I* and *II* have the same meaning as in Fig. 6. Curve *III* represents a comparison of the experimental data with Eq. (8) of the text.

lium acceptors. Although the good agreement of these two values is probably accidental, it suggests the desirability of extending the averaging procedure of Pippard and Twose to the two center conductivities $\sigma(R)$ calculated from the complete Kohn-Schechter acceptor wave functions so that also the absolute magnitude of the observed impurity conductivity can be compared with Twose's theory.

4. Discussion of the activation energy

To explain the temperature dependence of impurity conduction in the range of small impurity concentration, Mott suggested⁷ that the spacially fluctuating potential due to the ionized compensators requires thermal activation of carriers from the low-energy majority neighbors of the charged compensators. If the compensation ratio is small ($K < 0.1$) it seems reasonable to distinguish between "free majority sites" and "trap majority sites" which are separated by an average activation energy. Price²⁷ worked out the consequences of such a model. If K is large, however, each majority site has a near neighboring minority site and Price's considerations are no longer applicable. For this case, as Mott pointed out, an activation energy will still arise, since at low temperatures the carriers will seek out the majority sites of lowest energy from where they cannot move unless they absorb a phonon.

Using this model Twose calculated the root mean square energy difference between any two majority sites and found

$$E_{\text{rms}} = (2.28\pi K)^{\frac{1}{2}} N_{\text{maj}}^{\frac{1}{2}} e^2 / \kappa. \quad (9)$$

Substituting for the dielectric constant $\kappa = 16$ and for the compensation ratio $K = 0.40$ we obtain $E_{\text{rms}} = 9.44 \times 10^{-9} / r_A$ ev with r_A measured in cm. The relation between the activation energy ϵ_3 and E_{rms} has not been worked out. We obtain a fairly good fit with the experimental ϵ_3 values of the purer samples ($N_A < 4 \times 10^{15}/\text{cc}$) by taking $\epsilon_3 = \frac{1}{4} E_{\text{rms}}$.

Miller's theory yields an activation energy for the impurity conduction process without further assumptions. He obtains for *p*-Ge and $K = 0.40$

$$\epsilon_3 = 2.5 \times 10^{-9} r_A^{-1} \text{ ev.} \quad (10)$$

The values obtained from Eq. (10) are presented by the

dotted curve in Fig. 4. In the range ($r_A > 3.5 \times 10^{-6}$ cm) for which Miller's theory holds, the theoretical curve agrees remarkably well with the experimental data. It should be noted, however, that the value for ϵ_3 of sample 1-A is not quite certain and has to be reexamined.

V. CONCLUSIONS

By slow neutron bombardment and nuclear transmutation we obtained *p*-type germanium samples which are ideally suited for a quantitative investigation of impurity conduction. Since the compensation ratio is the same for the samples used in this study, the dependence of the resistivity and the activation energy of impurity conduction on impurity separation could be determined and compared with the theories of Miller and Twose. Despite the fact that the complicated acceptor wave functions lead to some unresolved computational difficulties, we can draw the following conclusions.

(i) Miller's theory seems to be very successful in calculating the activation energy ϵ_3 of the impurity conduction process at low impurity concentrations. The averaging procedure developed by Miller to account for the random impurity distribution, however, seems to over-estimate the contribution to the total resistivity of impurity pairs separated by more than the average distance.

(ii) Twose's theory yields an exponential decay of the acceptor wave functions which agrees very well with that expected from the Kohn-Schechter theory of the acceptor states. It also agrees well with the hydrogenic *s* functions which yields the experimentally observed acceptor ionization energy. The agreement is particularly good when the Twose-Pippard averaging procedure is used for the random impurity distribution.

Dislocation densities up to 10^4 per cm^2 do not affect impurity conduction. This fact confirms the original hypothesis that impurity conduction can arise from the interaction of impurities distributed at random throughout the crystal.

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²⁷ P. J. Price, I. B. M. J. Research Develop. 2, 123 (1958).