

# Impurity Band Conduction in Germanium and Silicon\*

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In this paper, we attempt to establish the idea of impurity band conduction on a firmer theoretical basis for germanium and silicon. Calculations by Baltensperger of energy bands arising from the impurities are adapted for these materials by replacing wave functions of impurity states with suitable hydrogenic approximations. These are used to estimate the concentration for which the impurity band substantially merges with the remainder of the conduction band, and this estimate is found to agree reasonably well with experiment. An estimate is also made of the range of concentrations for which the usual band type of theory might be applicable to electrons in the impurity band. It is found that approximately within this range the simple band theory does well for the impurity band. This, incidentally, high-

lights the necessity of taking into account conduction in impurity states for degenerate and near-degenerate samples even at relatively high temperatures. For concentrations lower than these a crude treatment of conduction is described which can account for the sharp increase in impurity band resistivity with decreasing impurity concentration, the importance of compensation in these samples, and even the order of magnitude of the resistivity. It does not, however, predict the correct temperature dependence for the resistivity, and a possible origin for this is suggested. The question of the sign of carriers in the impurity band is discussed, and it is shown that the sign reversal of thermoelectric power observed for the impurity band need not imply a change in sign of the effective mass.

## I. INTRODUCTION

THE idea of impurity band conduction was advanced by Hung<sup>1</sup> to explain the flattening of the resistivity and occurrence of a maximum in the Hall constant at low temperature in germanium samples.<sup>2</sup> Additional work by Fritzsche and Lark-Horovitz<sup>3</sup> and Fritzsche<sup>4</sup> put this idea on a firmer basis experimentally by elimination of a number of other possible explanations for these phenomena. It remains still to establish this explanation on a firmer theoretical footing and that is one of the purposes of the present paper. A major problem here is accounting for conduction in impurity states at the low concentrations involved; it is felt that sufficient information on the details of band structure and impurity states is now available to make real progress in this direction possible. A second purpose of this paper is to emphasize the fact that conduction in impurity states must be taken into account in the analysis of bulk properties in concentration and temperature ranges where this has not generally been done.

Part II and the first section of part IV will be concerned mainly with highly impure samples. It will be shown in part II just where the usual one-carrier theory is inadequate to explain the variation of Hall constant and Hall mobility with concentration and temperature. Part III deals with the energy level structure of impure material. A theoretical calculation of impurity band-width as a function of spacing between impurities has been carried out by Baltensperger assuming hydrogen-like impurities and distribution in a regular lattice. Neither of these assumptions is satisfied here, and the modifications which arise from dropping them will be

discussed. Estimates will be made of the concentrations in germanium and silicon above which: (1) the impurity band is merged with the conduction band, (2) the usual band picture might provide a fair approximation for electrons in the impurity band.

Conduction in impure samples will be taken up in part IV. The first section will deal with samples which lie in the concentration range selected by the two criteria of the preceding paragraph. It will be shown that the usual simple band treatment is capable of accounting in detail for the observations made on such samples. The last section of part IV will attempt to deal with some of the phenomena found at lower impurity concentrations. A crude theory of conduction, suggested by the importance of compensation in these samples, will be shown capable of explaining some of the experimental results for this concentration range. The interpretation of thermoelectric power measurements of Geballe and Hull and the sign of impurity band carriers will be discussed.

## II. DISCUSSION OF EXPERIMENTAL RESULTS<sup>5</sup>

In this section, we shall analyze experimental Hall and Hall mobility data for fairly impure samples on the basis of a one-carrier theory. This is equivalent to assuming that all electrons are in the conduction band, or that the impurity band electrons have properties identical with those of the conduction band electrons.<sup>6</sup> It will be shown where this is inadequate. This has been done to some extent by Hung and Gliessman, but the case they make can be strengthened.

It should be remarked first that for *p*-type germanium and silicon, even when all holes are in "the valence band," we must deal with two types with different

\* Some of this material was presented at the New York meeting of the American Physical Society, 1955 [see Phys. Rev. **98**, 1178(A) (1955)].

<sup>1</sup> C. S. Hung, Phys. Rev. **79**, 727 (1950).

<sup>2</sup> C. S. Hung and J. R. Gliessman, Phys. Rev. **79**, 726 (1950); **96**, 1226 (1954).

<sup>3</sup> H. Fritzsche and K. Lark-Horovitz, Physica **20**, 834 (1955).

<sup>4</sup> H. Fritzsche, Phys. Rev. **99**, 406 (1955).

<sup>5</sup> The notation used throughout will be that of P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).

<sup>6</sup> It is convenient to speak specifically in terms of electrons in much of what follows. The results are expected to apply to holes, *mutatis mutandis*.

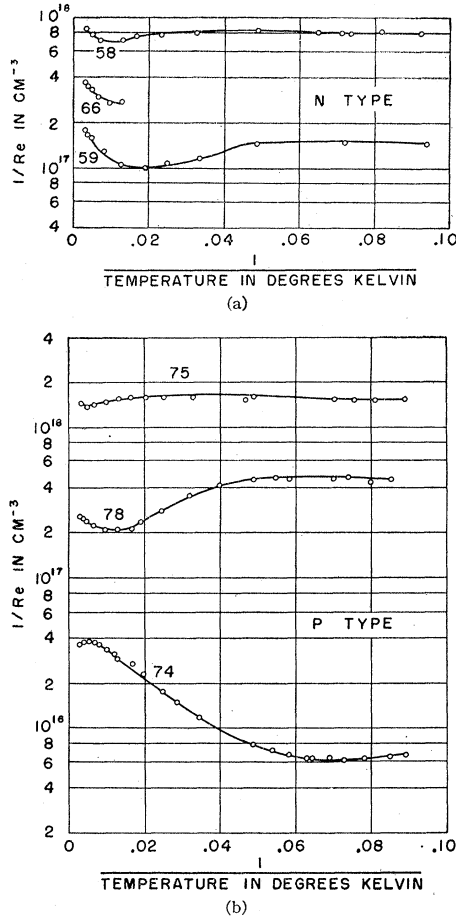


FIG. 1. (a) Reciprocal of product of Hall constant and charge on the electron *vs* reciprocal of absolute temperature for some *n*-type germanium samples. (b) Reciprocal of product of Hall constant and charge on the electron *vs* reciprocal of absolute temperature for some *p*-type germanium samples. Magnetic field intensity was about 3000 oersteds. The data were taken by P. P. Debye.

masses and mobilities. Since the constant energy surfaces of both holes have been shown to be approximately spherical near the band edge, it should be accurate enough for present purposes to take the low-field Hall constant as given by

$$R = -\frac{1}{e} \frac{n_1 \mu_1 + n_2 \mu_2}{(n_1 \mu_1 + n_2 \mu_2)^2} = \frac{\langle \mu_H \mu \rangle}{\langle \mu \rangle^2} \frac{1}{(n_1 + n_2)e}, \quad (1)$$

and the Hall mobility as:

$$R\sigma = \frac{n_1 \mu_1 + n_2 \mu_2}{n_1 \mu_1 + n_2 \mu_2} = \frac{\langle \mu_H \mu \rangle}{\langle \mu \rangle}. \quad (2)$$

Such information as there is on the two types of holes<sup>7,8</sup> indicates that  $\langle \mu_H \mu \rangle / \langle \mu \rangle^2$  is no larger than perhaps 3.

<sup>7</sup> Dresselhaus, Kip, and Kittel, *Phys. Rev.* **92**, 827 (1953); R. N. Dexter and B. Lax, *Phys. Rev.* **96**, 223 (1954).

<sup>8</sup> Willardson, Harman, and Beer, *Phys. Rev.* **96**, 1512 (1954).

It is then sufficiently accurate for our purposes to say that  $R \approx 1/(n_1 + n_2)e$ , and  $R\sigma$  represents the average mobility. The accuracy of these relations should improve as one goes beyond the low-field range, and they become exact in the limiting case of high fields. In what follows, therefore, we shall make no explicit distinction between the two types of valence band holes.

In the case of electrons in the conduction band there is evidence that the simple one-carrier theory for Hall effect is reasonably valid.<sup>9</sup>

We shall consider now experimental data for highly impure samples. Figures 1(a) and 1(b), 2(a) and 2(b) show some typical data for this range. The *n*- and *p*-type samples involved were made from germanium which had been carefully purified and then doped with arsenic or gallium, respectively.<sup>10</sup> Extensive study of other similarly prepared samples leads to the belief that these are to a high degree free of imperfections and impurities other than the ones intentionally added.

According to a theory based on one type of carrier then (i.e., electrons in the conduction band or holes in the valence band), the curves of Figs. 1(a) and 1(b) represent within a small factor the variation in carrier concentration with temperature. This factor can be expected to be a function of impurity concentration and temperature, and has not as yet been calculated in detail for the actual band structures involved. In prin-

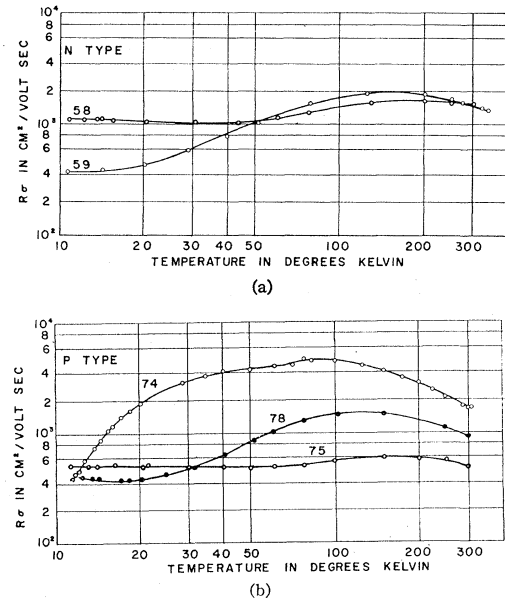


FIG. 2. (a) Hall mobility *vs* absolute temperature for the *n*-type germanium samples of Fig. 1(a). (b) Hall mobility *vs* absolute temperature for the *p*-type germanium samples of Fig. 1(b). Magnetic field intensity was about 3000 oersteds. The data were taken by P. P. Debye.

<sup>9</sup> See, for example, Debye and Conwell, reference 5.

<sup>10</sup> For a detailed description of sample preparation and experimental procedure see Debye and Conwell, reference 5. The samples were prepared and data taken at Bell Laboratories.

ciple, its inclusion could modify the shape of these curves, and such information as is available indicates that it does indeed make some minor changes. (See part IV.) Over-all, however, the variations in shape which accompany fairly small changes in temperature and concentration, particularly for the *p*-type case, are so large as to make it difficult to believe that its inclusion everywhere would have a significant effect. It is then necessary to explain peculiarities such as the existence of a low-temperature plateau at a concentration approximately one-tenth the room temperature value, or an apparent increase in carrier concentration with decreasing temperature. The presence of a large amount of another impurity of much lower activation energy might be invoked to explain the first, and perhaps a suitable temperature coefficient for the activation energy to explain the latter, but these are unlikely and artificial explanations. Similar data have been obtained for silicon.<sup>11,12</sup>

In Figs. 2(a) and 2(b) are Hall mobility *vs* temperature data for the same set of samples. The behavior of the Hall mobility at temperatures above about 100°K appears reasonable, qualitatively speaking, for samples with a mixture of lattice and impurity scattering. The relative flatness of the curves for the most heavily doped samples is presumably explained by the fact that they are in a transition region between Maxwell-Boltzmann statistics and Fermi-Dirac statistics.

Below about 30°K only impurity scattering need be considered in these samples. At the lowest temperatures obtained here,  $\mu_H$  of all the samples but 74 goes into a temperature-independent region indicating the onset of Fermi-Dirac statistics, where the impurity mobility is temperature-independent. It is notable that the curves for the different samples have crossed, so that in this region the samples with higher impurity content have higher mobility. This trend has been found also for silicon samples.<sup>11,13</sup>

As expected theoretically, the temperature of the transition to Fermi-Dirac statistics is lower the lower the impurity content of the sample. Sample 74, least heavily doped of the group, is still going down sharply at the lowest temperatures, showing no tendency yet to flatten. In the neighborhood of 11.5°K, the Hall mobility of this sample is changing with temperature as  $T^{+3.5}$ . Unfortunately, there was no *n*-type sample in this set with the proper concentration to show this steep slope. (Presumably one with concentration a little less than that of sample 59 would be suitable.) However, such a slope can be seen in some of the highly doped *n*-type silicon samples (as well as *p*-type), for example Pearson and Bardeen's sample *B*, Morin and Maita's sample 126. It is noteworthy that in all cases this slope is associated with samples having curves of

$1/Re$  *vs*  $1/T$  similar to that of 74. Further, for each sample the steep slope occurs in the neighborhood of the temperature associated with the minimum in  $1/Re$ , or what would presumably be part of a minimum if lower temperature data were taken. Samples with still higher impurity concentration do not show this steep a slope. However, it is also the case for these samples that the steepest slope of  $\mu_H$  *vs*  $T$  occurs in the temperature region of the minimum in  $1/Re$  for the particular sample.

Consider how these experimental results compare with the predictions of a one-carrier theory. On theoretical grounds the temperature dependence anticipated for impurity mobility is  $T^{+1.5}$ . Experimental indications are that this predicted temperature dependence is, if anything, steeper than the actual value.<sup>9</sup> There is no known scattering process for elemental semiconductors which leads to a temperature dependence as steep as  $T^{+3.5}$ .

The dependence on concentration of the mobility in the Fermi-Dirac region also cannot be explained by the usual theory. A formula for the impurity mobility valid in this region was derived by Mott<sup>14</sup> some years ago. This is:

$$\mu_I = -\frac{3\pi}{2} \frac{\hbar^3 \kappa^2}{m^{*2} e^3} \left[ \log \{ 1 + (24\pi^2 n)^{1/3} \lambda^2 \} - \frac{(24\pi^2 n)^{1/3} \lambda^2}{1 + (24\pi^2 n)^{1/3} \lambda^2} \right]^{-1}, \quad (3)$$

where  $\lambda$  is the screening length for the ion potential, which Mott evaluates in an approximate fashion, and the other symbols have the usual meaning. This result is identical with that obtained by extending the Brooks-Herring formula<sup>9</sup> into the Fermi-Dirac range. In the latter case the screening distance was taken as the Debye length. This can be generalized for the present case as follows:

$$\lambda = \left[ \frac{1}{3} \frac{\kappa m^* \langle v^2 \rangle}{4\pi n e^2} \right]^{1/2} = \left[ \frac{3^{1/2} \pi^{1/2}}{20} \kappa a_H^* n^{-1/3} \right]^{1/2}, \quad (4)$$

where  $a_H^*$  is the radius of the first Bohr orbit for an electron of mass  $m^*$ . The screening length employed by Mott is essentially of the same form, involving the same dependence on carrier concentration. It can be shown simply that Eqs. (3) and (4) predict an impurity mobility which decreases with impurity concentration,<sup>15</sup> contrary to the experimental results.

As seen in the data of Hung and Gliessman,<sup>1</sup> less impure samples show many of the features which have been remarked on for the highly impure ones. Curves

<sup>14</sup> N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

<sup>15</sup> Extension of the Conwell-Weisskopf formula into this range, carried out by V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **71**, 374 (1947), also gives a mobility which decreases with impurity concentration. For discussion see W. Shockley, reference 13, p. 281.

<sup>11</sup> G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

<sup>12</sup> F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

<sup>13</sup> W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 283.

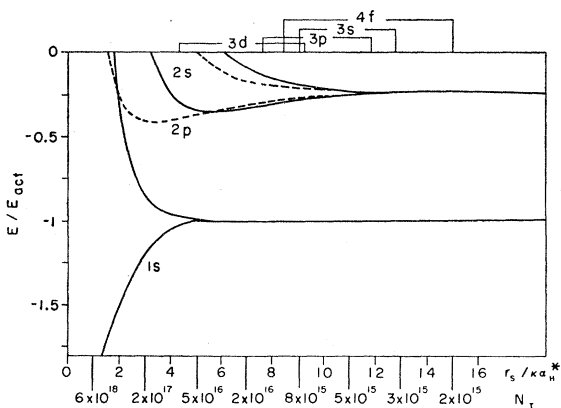


FIG. 3. Baltensperger's results for energy levels of impurities *vs* impurity spacing. The lower abscissa scale, representing impurity concentration for a dielectric constant of 16 and effective mass of  $m_0/4$ , has been added for illustrative purposes. At the top are indicated the radii of the atomic cell for which the edges of some further bands cross the value  $E=0$ .

of  $R\sigma$  *vs*  $T$  resemble that of 74 in that below a high-temperature region in which behavior is explainable by the usual theory they go into a region of steeper slope. This occurs at lower temperature than it does for 74, and the slopes are steeper.<sup>16</sup> Again, this steep slope occurs in the same temperature region as the minimum of  $1/Re$ .

### III. ENERGY LEVELS IN IMPURE MATERIAL

As a first step in a theoretical explanation of the results of the preceding section, we shall discuss the energy levels of a disordered substitutional alloy of germanium or silicon with one of the usual column III or column V impurities. Since a rigorous solution of this problem is not available, we shall begin by reviewing Baltensperger's solution for the case where the impurities are assumed to be on a regular lattice.<sup>17</sup>

To obtain the energy bands of the impurity lattice Baltensperger uses a cellular method. The atomic polyhedra surrounding each impurity are approximated by spheres of radius  $r_s$  such that  $(4/3)\pi r_s^3 = 1/N_I$ , where  $N_I$  is the number of impurities per  $\text{cm}^3$ . Within each sphere the bound electron wave function and energy are assumed to satisfy the Wannier or effective mass equation for the simple model of the band structure.<sup>18,19</sup> The potential in the cell is taken as  $-e/\kappa r$ , which is, of course, not correct very close to the ion. It is assumed that the bottom and top of the bands are characterized by periodic and antiperiodic wave functions, respec-

tively. The energy values satisfying the resulting boundary conditions, and thus presumably representing the band edges, are plotted as a function of  $r_s$  (measured in units of  $\kappa a_H^*$ ) in Fig. 3. The results are qualitatively as expected for such a calculation. At infinitely large distance between impurities there is the complete set of hydrogenic levels. As the distance between impurities decreases, the wave functions of successively lower excited levels overlap and form bands. The ground state spreads visibly on this scale, forming what is usually called the impurity band, at  $r_s \sim 5\kappa a_H^*$ .

This calculation does not explicitly mention the conduction band of the underlying medium. As discussed by Slater, for example, the effect of the Coulomb potential arising from the donor ions is to perturb all the conduction band states, the lowest ones most.<sup>20</sup> The levels of Fig. 3 have presumably been pulled down from the conduction band. At low impurity concentration, on the right side of Fig. 3, say, we should be able to neglect the effect of the impurities on the conduction band in the usual sense that we describe the levels as constituting an unaffected conduction band starting at  $E=0$  (at least approximately), with some discrete levels and perhaps bands below. As the impurity concentration increases, more levels are pulled down and presumably the remaining conduction band levels are more perturbed. In any case, it appears that the impurity band remains separated from the other levels at least down to  $r_s$  of the order of  $2\kappa a_H^*$ . At  $r_s \sim \kappa a_H^*$  the separation has evidently vanished and this group of levels has merged with the remainder.

In view of the use of a hydrogenic potential and the neglect of randomness, the effort involved in obtaining results analogous to those of Fig. 3 for the actual band structures is difficult to justify. It appears practical therefore to make use of Baltensperger's results, and this will be done in the following way. Hydrogenic approximations valid for the ground state at large  $r_s$  will be set up. Excited states will not be considered explicitly since they mostly remain very close to the conduction band or overlap it. For  $n$  and  $p$  germanium and  $n$  silicon, wave functions for the ground state obtained by variation method are available as a guide. The hydrogenic approximations supply a value of  $\kappa a_H^*$  which will be used with Baltensperger's results to trace the behavior of the energy to smaller  $r_s$ . Errors due to neglecting the deviation from the hydrogenic potential, and to randomness, will then be examined.

The variational wave functions for the ground state consist of a sum of terms which, apart from periodic modulating factors, decrease approximately exponentially with distance. In the case of electrons bound to donors, this decrease is essentially given by

$$\exp\{-[\alpha^2 z^2 + \beta^2(x^2 + y^2)]^{1/2}/\kappa a_H^*\},$$

<sup>16</sup> This is not shown in Fig. 9 of Hung and Gliessman, reference 1, because  $R\sigma$  is not plotted to low enough temperatures for samples purer than SB-3.

<sup>17</sup> W. Baltensperger, *Phil. Mag.* **44**, 1355 (1953).

<sup>18</sup> See, for example, J. M. Luttinger and W. Kohn, *Phys. Rev.* **97**, 869 (1955).

<sup>19</sup> More correctly, according to the formulation of effective mass theory by Luttinger and Kohn, the bound electron wave function for the simple model is of the form  $F(r)\psi_c(r)$ , where  $F(r)$  is the solution of the Wannier equation and  $\psi_c(r)$  is the Bloch function at the band edge.

<sup>20</sup> J. C. Slater, Technical Report No. 5, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, December 15, 1953 (unpublished).

where  $\alpha$  is between 2 and 3 times as large as  $\beta$ , and  $x$  and  $y$  are transverse directions.<sup>21</sup> It appears reasonable to replace this with the hydrogenic function having an effective mass ratio  $m^*/m_0 = \beta$ . This of course, overestimates somewhat the extent in directions other than the transverse ones. It should lead, therefore, to a somewhat low estimate of the desired concentrations but this error should not be large. In the case of bound holes in germanium the factors giving the decrease with distance are of the form<sup>22</sup>  $e^{-r/r_1}$  and  $r^2 f(\theta, \phi) e^{-r/r_2}$ , where  $r_2$  is about  $0.8r_1$ . Very crudely we shall approximate this wave function by the hydrogenic function with  $m^*/m_0 = \kappa a_H / r_1 \approx 0.2$ . It is interesting to note that this is very close to the mass for which the hydrogen model gives the observed activation energy. Actually, the  $e^{-r/r_2}$  terms in the wave function are comparable in size to the  $e^{-r/r_1}$  terms out to  $r$  greater than  $5r_1$  because of the  $r^2$  factor in the former. Thus the bound hole wave function falls off less rapidly with distance than the hydrogenic approximation, and this should cause estimates of the desired concentrations to be somewhat high.

Since solutions are not yet available for bound holes in silicon, for purposes of a crude estimate we shall use the hydrogenic function with the  $m^*/m_0$  value required to give the observed activation energy for acceptors in silicon. The germanium experience suggests that this should not be too bad. Unfortunately, there is considerable variation in activation energy among the column III acceptors. Since the measurements available are on boron-doped silicon we choose the  $m^*/m_0$  value appropriate to boron, 0.5. This is also equal to the heavy hole mass.

The masses which have been selected for the hydrogenic approximations to the bound wave functions are listed in Table I. We shall now use these, in conjunction with Baltensperger's results, to estimate the concentration for which the impurity band merges with the conduction band. According to the discussion earlier in this section this should occur around  $r_s = \kappa a_H^*$ . The concentrations which satisfy the condition  $r_s = \kappa a_H^*$  are listed in the third column of Table I. The  $>$  and  $<$

signs indicate where it is thought that these concentrations have been under- or overestimated because of the choice of the approximating function. These errors should, however, not be large.

Another quantity of interest is the lowest concentration at which a band picture along the usual lines might provide a good description for electrons in the impurity band. This could be called, very loosely, the concentration for "formation of an impurity band."<sup>23</sup> As a rough guide here, and probably in the nature of a lower limit, we have listed in Table I the concentrations for which the width of the impurity band, as calculated by Baltensperger, is of the order of  $kT$  at  $10^\circ\text{K}$ . (This is in the temperature range where conduction in impurity states is generally predominant.) This corresponds to  $r_s$  around 4 or  $5\kappa a_H^*$ .

Discussion so far has been confined to the case of a regular arrangement of impurities. No calculation of energy *vs*  $r_s$  is available for a random arrangement, but there are some good qualitative guides to the results. Let us consider these for the case of the lowest impurity level. For either a regular or random arrangement of  $N_I$  impurities there are, for very large  $r_s$ ,  $2N_I$  localized levels, all of the same energy.<sup>24</sup> When  $r_s$  is small enough so that there is appreciable overlapping of electron wave functions on adjacent impurities the  $2N_I$  energy levels split. The resulting "band" cannot be expected to have well defined edges in the random case because these are characteristic of a periodic arrangement. For small overlapping or interaction, however, it is to be expected that most of the levels would be close to the original energy. These features have been found by James and Ginzburg in calculations for a comparable one-dimensional random case.<sup>25</sup> They find that the density-of-states curve still shows a narrow maximum around the original energy, but there are long tails to both low and high energy, the latter overlapping the conduction band. Thus, as compared with the density of states for a regular distribution, the curve for the random arrangement of the same impurities should be

TABLE I. Estimated impurity concentrations for "formation of an impurity band," and for its overlap with the conduction band.

Case	$m^*/m_0$ of hydrogenic approximation	$N_I$ for overlap $\text{cm}^{-3}$	$N_I$ for "band formation" $\text{cm}^{-3}$
<i>n</i> -Ge	0.13	$>9 \times 10^{17}$	$>1 \times 10^{16}$
<i>p</i> -Ge	0.2	$<3 \times 10^{18}$	$<5 \times 10^{16}$
<i>n</i> -Si	0.27	$>2 \times 10^{19}$	$>1 \times 10^{17}$
<i>p</i> -Si	0.5	$<1 \times 10^{20}$	$<1 \times 10^{18}$

<sup>21</sup> C. Kittel and A. H. Mitchell, Phys. Rev. **96**, 1488 (1954); M. A. Lampert, Phys. Rev. **97**, 352 (1955).

<sup>22</sup> W. Kohn and D. Schechter, Phys. Rev. **99**, 1903 (1955). The author is indebted to Dr. Kohn for making these results available before publication.

<sup>23</sup> For values of  $r_s$  greater than this, in the case of uncompensated material it would be reasonable to consider the electrons localized and use Heitler-London wave functions. (See N. F. Mott, in "Semi-Conducting Materials," Butterworths Scientific Publications, London, 1951). This is not necessarily the case, however, for compensated material, because there the existence of empty sites should permit motion of the electrons from one ion to another even at much larger values of  $r_s$ . Thus the feature of extended rather than localized wave functions would be valid at much lower concentrations than those "for band formation" in compensated material. It is nevertheless not likely that other features of the usual band picture would apply. Specifically, at low temperature one would not expect more than one electron at a time on a donor ion, which, of course, is permitted by the usual band picture. From this point of view one may consider the figures in the last column of Table I as rough measure of the concentration below which electron correlations are important enough to prevent the accumulation of excess negative charge on the donor "atoms."

<sup>24</sup> More generally, the number of levels is  $N_I$  times the degeneracy of the ground state. This may be greater than 2.

<sup>25</sup> H. M. James and A. S. Ginzburg, J. Phys. Chem. **57**, 840 (1953).

more diffuse—broader, flatter, and without distinct edges. It will nevertheless be convenient to speak of the group of states arising from the lowest discrete state as the impurity band.

Consider now the effect of randomness of the arrangement on the concentrations listed in Table I. It has been pointed out by Baltensperger that disorder will increase the average interaction between electrons on different impurities over what it would be for a regular arrangement. This suggests that both the concentrations calculated should be lower for a random arrangement.<sup>26</sup> The amount of this lowering is difficult to estimate. As will be seen in part IV, there is no reason to believe that it is more than an order of magnitude. It should be noted also that the implications of the concentration “for band formation” must necessarily be somewhat modified for a random arrangement. Not all features of the usual band picture can be expected to apply in a random case. For example, the one-electron wave functions cannot correctly be taken in the Bloch form. It is therefore more suitable for this case to consider this concentration as indicating the lower limit for validity of such band features as extended rather than localized wave functions for uncompensated material<sup>28</sup> and the relative unimportance of electron correlations.

There is another effect, so far neglected, which gives a systematic error in the other direction. This is the deviation of the potential from the hydrogenic one at small  $r$ , which causes an additional concentration at small  $r$  with consequent diminution of the wave function at large  $r$ . Thus the hydrogenic approximations which have been set up overestimate the correct wave functions at large  $r$ , and thus the overlapping. From this point of view the concentrations listed in Table I are too low.

It is possible to get an idea of the importance of this effect from the difference between the variational energy for the ground state (calculated for the hydrogenic potential) and the activation energy obtained, for example, from Hall data.<sup>27</sup> In the case of germanium these differences are fairly small for the column III acceptors and for Sb. They are considerable for P and As, of the order of 30%. For column V donors in silicon the differences are also considerable, being least for Sb. Although the variation energy has not yet been calculated for acceptors in silicon, it is to be anticipated from the observed large variations in activation energy that the differences will be considerable here also. We conclude that the underestimate of the concentrations in Table I from this effect should not be large for Sb and column III acceptors in germanium, but may be considerable for the other cases. Presumably the discrepancy will be larger the larger the binding energy for the particular impurity. We have here then a source

of systematic differences in impurity band conduction for different impurities.

From all of the foregoing, it is clearly not possible to tell whether the concentrations of Table I are systematically under- or overestimated. In fact, they may conceivably be too high for some impurities, and too low for others. However, it does seem reasonable to expect that these concentrations will serve fairly well as guides in understanding the experimental results. This is the more true since the criteria of merging of the bands or “impurity band formation” are of course loose enough so that they do not single out particular concentrations, but rather a range of concentrations in the neighborhood of those chosen for Table I.

#### IV. CONDUCTION IN IMPURE MATERIAL

A good deal has been done in the past to show<sup>1-4</sup> that a simple two-band theory will go far in explaining the type of Hall and resistivity results we have been discussing. Applicability of band theory to carriers in the impurity band at the concentrations involved had not, however, been established. From the results of the last section it appears reasonable to apply band theory to carriers in the impurity band down to concentrations of the order of those listed in the last column of Table I. Of course, the detailed predictions of a band theory should depend on the distribution-in-energy of the states in the band, etc., and this has not been worked out. It seems reasonable, therefore, to compare experimental results with the predictions of band theory for the simplest case—that of spherical constant energy surfaces—and this will be done in the first part of this section. In this, two-band theory will be applied to the study of  $R$  and  $\mu_H$  of samples with impurity concentration greater than those for “impurity band formation.” The germanium samples discussed in part II all fall in this range, although sample 74 is close to the lower limit. This study will also serve to highlight the necessity for taking into account impurity band conduction in discussing bulk properties of highly impure samples.

The last part of this section will be concerned with some aspects of conduction in impurity states at lower impurity concentrations, where we have reason to believe we are dealing with a narrow impurity band. Thermoelectric power measurements of Geballe and Hull and their implications for the sign of the carriers in the impurity states will be discussed. It will be shown that some of the observations in such samples can be understood on the basis of a simple and crude model of conduction. Possible explanations for some of the peculiarities in temperature dependence of the Hall constant and resistivity will be presented.

#### Properties of Heavily Doped Samples

We shall present now an explanation in terms of a two-band theory of the apparently anomalous results

<sup>26</sup> It has also been pointed out by P. Aigrain, *Physica* **20**, 978 (1954), that the concentration at which extended wave functions are valid should be lower for a random arrangement.

<sup>27</sup> T. H. Geballe and F. J. Morin, *Phys. Rev.* **95**, 1085 (1954).

discussed in part II. Consider the curves of Hall mobility *vs* temperature. Where  $\mu_H$  is independent of temperature, or Fermi statistics are valid, the electrons have more or less sunk into the impurity levels and we are observing the Hall mobility characteristic of these levels. At the higher temperatures the data should essentially represent the Hall mobility of the conduction band. The flatness of the  $\mu_H$  *vs*  $T$  curves for samples 75 and 58 means that the distinction between impurity levels and conduction band levels has more or less vanished. The concentration for which these approximately flat curves are obtained is  $10^{18}/\text{cm}^3$  in both  $n$  and  $p$  germanium, around  $10^{19}/\text{cm}^3$  in both types of silicon. These figures agree quite well with the theoretical predictions in Table I giving the concentrations for merging of the bands. Sample 74, on the other hand, corresponds to the case of a narrow impurity band according to the figures of Table I.

Additional support for this characterization of the impurity bands in the different samples comes from the spin resonance experiments of Fletcher *et al.*<sup>28</sup> Absorption lines corresponding to transitions among hyperfine levels of electrons bound to donors are seen in Si samples up to concentrations of about  $10^{18}/\text{cm}^3$ . At higher concentration these hyperfine lines disappear, being replaced by a single line which has been attributed to conduction electrons. Observation of the hyperfine lines requires that electrons be fairly well localized around the donors, not moving too rapidly from one to another.<sup>29</sup> It is to be expected then that the highest concentration for which they are observed be approximately equal to the concentration "for impurity band formation." Comparison with Table I shows that this is indeed the case for donors in silicon. In germanium the hyperfine lines are not observed at  $10^{18}/\text{cm}^3$ , which also would be expected from the previous discussion. To obtain electrons sufficiently localized for hyperfine lines to be observed should require a concentration below  $10^{17}/\text{cm}^3$  in the case of germanium.

This characterization makes it possible to explain the observation of increasing low temperature Hall mobility with increasing impurity concentration below  $10^{18}/\text{cm}^3$  in germanium as due to increasing overlap of electron wave functions on adjacent impurities. (This corresponds to the decrease in  $m^*$  of a conventional narrow band with increasing band width.) Of course this will be affected, and perhaps enhanced, by the changing

character of the wave functions with increasing overlap of conduction band and impurity band.

For the cases where overlapping is sufficiently small that conduction band and impurity band are more or less distinguishable, we shall apply the simple two-band formulas of part II. The subscript 1 will now denote carriers in the conduction band, and 2 carriers in the impurity band. The fact that the general shape of the  $R$  *vs*  $1/T$  curves is given by (1) has been discussed elsewhere. It is worth pointing out that (1) can account for further details of the shape also. Consider samples  $p$ -78 and  $n$ -59. At  $300^\circ\text{K}$ , both are in the temperature range for which (1) gives  $1/Re \simeq (\mu_1/\mu_{1H})|N_D - N_A|$ . Below about  $20^\circ\text{K}$ , they show a plateau for which, according to (1),  $1/Re = (\mu_2/\mu_{2H})|N_D - N_A|$ . The values of  $\mu_H/\mu$  appropriate for these samples at  $300^\circ\text{K}$  have been obtained, at least approximately, by Prince.<sup>30</sup> For  $p$ -type material at this concentration the factor is about 2. For  $n$ -type material it is a little less than 1. At the low-temperature end when the carriers are in impurity levels and degeneracy has set in, theory based on spherical constant energy surfaces predicts that  $\mu_H/\mu = 1$ . Thus if this theory is valid for the impurity band and we are indeed dealing with a constant total number of carriers,  $1/Re$  at  $300^\circ\text{K}$  for  $p$ -type samples should be about  $\frac{1}{2}$  its value at the low-temperature end, and for  $n$ -type samples a little greater than its value at the low-temperature end. This is in fact what is seen experimentally. There is additional and more direct evidence in the case of the  $p$ -type sample, 78, that  $\mu_H/\mu$  for the impurity band is unity. This sample is in the concentration range for which a value of the drift mobility is available, and the number of carriers computed from  $\sigma/e\mu_d$  is approximately equal to  $1/Re$  at the low-temperature end.

Some simple relationships between the depth and position of the minima in  $1/Re$  *vs*  $T$  and impurity concentration (or, more accurately,  $|N_D - N_A|$ ) can be

<sup>28</sup> Fletcher, Yager, Pearson, Holden, Read, and Merritt, *Phys. Rev.* **94**, 1392 (1954); Fletcher, Yager, Pearson, and Merritt, *Phys. Rev.* **95**, 844 (1954).

<sup>29</sup> More quantitatively, the hyperfine lines should be wiped out when the jump frequency is of the order of the energy interval between hyperfine levels divided by  $\hbar$ . For As-doped silicon this condition leads to a jump frequency of  $10^8 \text{ sec}^{-1}$ . It is of interest to compare this with the value calculated from the theory of part IV. For a concentration of  $10^{18}/\text{cm}^3$  and the  $m^*$  value of Table I this theory predicts a jump frequency of  $10^{12} N_A/N_D \text{ sec}^{-1}$ . To obtain agreement  $N_A$  must be  $10^{14}/\text{cm}^3$ , which seems low for these samples. However, as discussed elsewhere, it is likely that use of the  $m^*$  value of Table I leads to an overestimate of the overlapping and of the jump frequency for As donors in Si.

<sup>30</sup> This factor is plotted as a function of impurity concentration in Fig. 11 of the paper by M. Prince, *Phys. Rev.* **92**, 681 (1953). It has been obtained by dividing the experimental values of  $R\sigma$  by the drift mobility calculated for majority carriers from that measured for minority carriers. Unfortunately, this latter calculation is to some extent uncertain because it involves a correction for impurity scattering which has been made on the basis of the simple model of the band structure. Within this limitation, it is clear in the case of electrons that  $\mu_d$  obtained in this way should equal conductivity mobility, so that  $R\sigma/\mu_d$  represents the desired  $R(ne)$ , or  $\mu_H/\mu$ . In the case of holes this is not immediately clear because of the complication of the two types of holes. From the evidence cited previously for approximately equal relaxation times of the two holes and failure to detect any effect of two holes in drift experiments [J. Harrick, *Phys. Rev.* **98**, 1131 (1955)], it is reasonable to conclude that interband transitions take place in a time very short compared to the time of drift in a drift mobility measurement. In that case the measured  $\mu_d$  should represent  $(n_1\mu_1 + n_2\mu_2)/(n_1 + n_2)$ . Then  $\sigma/e\mu_d$  should again equal total hole concentration, and  $R\sigma/\mu_d$  should equal  $R(n_1 + n_2)e$ , or the desired  $\mu_H/\mu$  for this case. This is still subject, of course, to the uncertainty mentioned previously. Note also that, although the hole mobilities are probably small enough in these samples so that there is little magnetic field dependence of  $R$  or  $\mu_H$ , the values of  $R$  for Prince's results were taken at the same magnetic field strength as that used for Debye's results.



derived from (1) if we make the assumptions that  $\mu_1/\mu_2$ , to be denoted by  $b$ , is independent of temperature, and  $\mu_H/\mu=1$ . We find then that the minimum occurs at the temperature for which  $n_1$  has dropped to  $1/(b+1)$  of the exhaustion value for the sample, or when  $n_1\mu_1=n_2\mu_2$ . The ratio of  $1/Re$  at the minimum to its value at exhaustion ( $\simeq |N_D-N_A|$ ) is given by  $4b/(b+1)^2$ . Since  $b$  increases as impurity content decreases, it is evident that these relationships predict the deepening and shift of the minima to lower temperatures as the samples grow purer. It might be noted that it is reasonable to expect some features of this behavior even when this sort of band treatment is not good for the impurity states. It should in any case be true if there is any conduction in impurity states that eventually, as one goes down in temperature,  $1/Re$  stops decreasing, having at least a local minimum. Further, the smaller the conductivity in impurity states, the more electrons must fall out of the conduction band before the impurity band conduction takes over. This will ensure deepening and shifts of the minima with decreasing impurity band conductivity for lower concentrations also.

From the minimum and exhaustion values of  $1/Re$  one obtains, using the relationships of the last paragraph,  $b \simeq 5$  for samples 59 and 78. This appears consistent with the observed  $\mu_H$ . For sample 74 one obtains  $b \simeq 25$ .

The behavior of  $\mu_H$  vs  $T$  in this simple two-carrier model is given by (2). In the region where  $n_1\mu_1 \sim n_2\mu_2$ ,  $R\sigma$  represents more or less a weighted average of the two mobilities, and its temperature variation reflects the rate at which carriers fall out of the conduction band as well as the temperature dependence of the individual mobilities. It is apparent that this temperature variation could be much steeper than that of the individual mobilities in a case where  $\mu_1 \gg \mu_2$ . This then provides an explanation for the steep slopes in  $\mu_H$  vs  $T$  remarked on in part II. These were observed to coincide with the region of the minimum in  $1/Re$  vs  $T$ , which is just the region where  $n_1\mu_1 \sim n_2\mu_2$ .

Because of the many variables it is difficult to extract quantitative information from  $\mu_H$  vs  $T$  in this region. With the same simplifications mentioned previously it can be shown that at the temperature for which  $1/Re$  has its minimum,  $\mu_H = [(b+1)/(2b)]\mu_1 = [(b+1)/2]\mu_2$ . Thus, in the case of a sample with large  $b$ , such as 74, at the temperature of the minimum  $\mu_H$  has fallen only to half of  $\mu_1$  and is still many times  $\mu_2$ .

Below the concentration range considered in this section (in fact, possibly even at the concentration of sample 74) there is evidence that the predictions of the simple band picture do not hold for the impurity levels. Fritzsche<sup>4</sup> has found that at about  $6 \times 10^{16}/\text{cm}^3$  and below, in both Ga- and Sb-doped Ge,  $R$  and  $\sigma$  of the impurity band do not go to constant, temperature-independent values but continue to increase with decreasing temperature.

More will be said about conduction at these lower

concentrations in the next section. We conclude here that: (1) the predictions of Table I are reasonably well borne out; (2) a simple band treatment of conduction in impurity states does very well qualitatively and even to some extent quantitatively in roughly the concentration range indicated in Table I. More precisely, this range is about  $8 \times 10^{16}/\text{cm}^3$  to  $10^{18}/\text{cm}^3$  in Ge. For Si an upper limit of  $10^{19}/\text{cm}^3$  is indicated, but not enough data are available to establish the lower limit clearly. It is likely that the Table I estimate of this lower limit is low for Si, probably more so than for Ge, because the concentrating effects of the deeper well at  $r=0$  seem generally larger for Si. This, of course, would be expected from the smaller value of dielectric constant and the larger effective masses.

### Properties of Less Impure Samples

Geballe and Hull have investigated<sup>31</sup> the thermoelectric power, to be denoted by  $Q$ , of a set of silicon samples in the range  $15^\circ\text{K}$  to  $350^\circ\text{K}$ . They find that samples with about  $10^{19}$  impurities per  $\text{cm}^3$  have the same sign of  $Q$  throughout this temperature range. In both an  $n$ - and a  $p$ -type sample, with about  $10^{18}$  impurities per  $\text{cm}^3$ , they find a change in the sign of  $Q$  at low temperature. The sign reversal occurs at a temperature for which  $1/Re$  of these samples has stopped decreasing and is approaching a minimum, thus a temperature for which the conductivity of the impurity band is comparable to that of the conduction band. For one of these samples Hall data are available to as low a temperature as the thermoelectric data and they show no sign change. It is, of course, conceivable that this could occur at a lower temperature. However, Hall data on Ge samples over a wide range of impurity concentrations and temperatures have never shown a sign reversal. Another interesting finding of this work is that addition of sufficient minority impurity to produce a very highly compensated sample seems to eliminate the sign change.

The product  $QT$  is equal to the energy transmitted per second per unit current when the energy zero is taken as the Fermi level, to be denoted by  $E_F$ . In order to understand the above results, we shall consider the location of the Fermi level in these samples in the temperature range concerned.

At a concentration of  $10^{18}/\text{cm}^3$  in Si, according to the evidence of the observation of hyperfine structure and the depth of the dips in  $1/Re$  vs  $1/T$ , we should be dealing with a narrow impurity band and fairly well localized electrons. In that case it is not correct, as pointed out by Slater,<sup>32</sup> to say that in the limit of low temperatures the lowest  $N_I$  of the  $2N_I$  states in the band will be occupied. Rather, it is necessary to use all of the states in the band in making up a wave function.

To obtain the location of the Fermi level, at least

<sup>31</sup> T. H. Geballe and G. W. Hull, Phys. Rev. **98**, 940 (1955).

<sup>32</sup> J. C. Slater, Revs. Modern Phys. **25**, 199 (1953).



approximately, we shall neglect the width of the donor band and use the usual expression for localized electrons:  $n_D/N_D = [1 + g_D^{-1} \exp(E_D - E_F)/kT]^{-1}$ , where  $n_D$  is the number of electrons bound to donors,  $g_D$  and  $E_D$  the degeneracy and energy of the donors, respectively. (As before, we shall assume  $g_D = 2$  in what follows.) For the  $n$ -type sample which showed the reversal, sample 126,  $N_D \simeq 10^{18}/\text{cm}^3$  and it is quite unlikely that  $N_A$  is greater than  $10^{16}/\text{cm}^3$ . For the latter value of  $N_A$ , at temperatures low enough so that few electrons are left in the conduction band, the equation above leads to  $E_F \simeq E_D + 4kT$  for sample 126. For the highly compensated  $n$ -type sample, 563, which did not show the reversal,  $N_D - N_A = 1.25 \times 10^{17}/\text{cm}^3$  and Geballe and Hull estimate  $N_A = 1 \times 10^{18}/\text{cm}^3$ . This leads to  $E_F \simeq E_D - 3kT$  at low temperatures for sample 563.

At 15°K in sample 126, even if we allow for an impurity band width of a few  $kT$ , the Fermi level should be above the impurity band, or at least above most of the electrons in it. As the temperature goes up the Fermi level in this sample rises, probably not as high as the edge of the conduction band, and then goes down again. Thus at high temperature when the carriers are in the conduction band  $E_F$  should lie below them, and we expect the usual negative sign of thermoelectric power. When the carriers are in the impurity band  $E_F$  should lie above them, producing a sign reversal of  $Q$ . In the highly compensated sample, 563, the Fermi level should be below the impurity band at all temperatures so no sign reversal is expected.

If this is the correct explanation, the thermoelectric results do not imply a change of sign of the effective mass of carriers within the impurity band, and there is no inconsistency between thermoelectric and Hall data. It then seems unlikely that such a sign change occurs, but details of the transport process for impurity band carriers should be better understood before this is concluded definitively. It should be said that currently there is no reason to believe that such a sign change will occur for a completely disordered array. The usual proof of its occurrence is based very directly on the periodicity of the atomic arrangement and the resulting existence of forbidden energy regions. Still, perfect periodicity is not a necessary condition since hole conduction has been found in some liquids. Thus local order of some degree is apparently a sufficient condition. That it is also a necessary condition seems likely, but still remains to be proved.<sup>33</sup>

In looking over  $1/Re$  vs  $1/T$  of Ge samples doped with different impurities, one finds some characteristic differences. For example, in the case of  $n$ -type material, As-doped samples show larger dips than Sb-doped

samples of the same  $N_D - N_A$ . This can be seen by comparing As-doped sample 61 of P. P. Debye and sample Sb-19-2 of Fritzsche.<sup>4</sup> Similar differences can be seen for  $p$ -type Ge. Ga-doped samples show characteristically deeper dips than In-doped samples.<sup>4</sup> As discussed in the last section, deeper dips should indicate less conductivity in the impurity band. A reason for such differences was suggested in part III—namely, differences in overlapping of wave functions of electrons bound to neighboring impurities as a result of different potential wells at the various impurities. It would be expected that such differences would be correlated with differences in binding energy. The As and Sb differences might be an example of this effect, since the binding energy of electrons to As donors is 30% higher than that for Sb donors. It is most unlikely, however, that the difference between Ga and In arises from this source. The difference in binding energy is very small, and furthermore in the wrong direction. It has been suggested by Fritzsche and Lark-Horovitz that it results from the greater degree of compensation, i.e. the greater minority impurity content, of In-doped samples compared with Ga-doped samples of the same  $|N_D - N_A|$ . This may well be a factor in the difference between As- and Sb-doped samples also. The segregation coefficient of Sb in Ge is about one-tenth that of As in Ge,<sup>34</sup> making it likely that Sb-doped samples will have a higher impurity background than As-doped ones.

Electron correlations should be important in these samples since we are dealing with narrow impurity bands. It is not surprising then that compensation should greatly enhance conduction. A crude treatment of impurity band conduction suggested by this is described in the following paragraphs.<sup>35</sup>

Consider that as a result of compensation there are  $N_{\min}$  donors out of a total of  $N_{\text{maj}}$  without a bound electron. We shall assume that  $N_{\min} < N_{\text{maj}}/2$ . An electron bound to one donor ion can tunnel over to an adjacent empty one. This process can also be thought of as diffusion of the ionized donors. To obtain the jump frequency, the system of the two neighboring donor ions and an electron was treated like a hydrogen molecule-ion. For this system the rate at which the electron oscillates between the ions is given by  $1/h$  times the energy difference,  $\Delta E$ , between the symmetric and antisymmetric combination of  $\psi$ 's localized on each ion. The diffusion constant for the process is then  $4r_s^2 \Delta E/h$ . Using the Einstein relation, we obtain a conductivity

$$\sigma = N_{\min} (e^2/kT) (4r_s^2 \Delta E/h). \quad (5)$$

In this form the expression is valid for either  $n$ - or  $p$ -type material. For the large  $r_s$  values of interest

<sup>33</sup> The case of Te is an interesting one here. Just above the melting point  $R$  and  $Q$  remain positive [A. Epstein and H. Fritzsche, Phys. Rev. **94**, 1426 (1954)], and conductivity varies exponentially with  $1/T$ , the slope corresponding to the forbidden band width of solid Te [V. A. Johnson, Phys. Rev. **98**, 1567 (1955)]. With increasing temperature  $R$  and  $Q$  decrease until they become negative and the conductivity becomes metallic.

<sup>34</sup> See J. A. Burton, Physica **20**, 845 (1954), for references.

<sup>35</sup> A similar treatment was used by C. Zener, Phys. Rev. **82**, 403 (1951), for a somewhat different case.

TABLE II. Calculated degree of compensation for some germanium samples.

Sample	$ N_D - N_A $ cm <sup>-3</sup>	$\rho$ at 4°K ohm-cm	$N_{\min}/N_{\text{maj}}$ from (8)	$N_{\min}/N_{\text{maj}}$ from Fritzsche
Ga-1	$4 \times 10^{15}$	$1 \times 10^6$	2%	3%
In-2	$4 \times 10^{15}$	$3 \times 10^4$	10%	35%
In-1	$1 \times 10^{16}$	$1 \times 10^7$	25%	30%

here<sup>36</sup>:

$$\Delta E \approx 8(r_s/\kappa a_H^*) E_{\text{act}} \exp(-2r_s/\kappa a_H^*), \quad (6)$$

where  $E_{\text{act}}$  denotes the activation energy. If we neglect the volume occupied by the minority impurities, and a constant factor not very different from 1, we obtain the following for the impurity band resistivity:

$$\rho \approx (N_{\text{maj}}/N_{\min})(\hbar kT/16\kappa E_{\text{act}}^2) \exp(2r_s/\kappa a_H^*). \quad (7)$$

For Ge, at 4°K this gives a resistivity in ohm-cm:

$$\rho \approx 5 \times 10^{-5} (N_{\text{maj}}/N_{\min}) \exp(2r_s/\kappa a_H^*). \quad (8)$$

Equation (7) shows directly the importance of compensation in the factor  $N_{\text{maj}}/N_{\min}$ . It predicts an additional effect of compensation through the dependence on  $r_s$ . From the derivation of (7),  $r_s$  refers to the distance between majority impurities. Thus, for two samples of the same  $|N_D - N_A|$ ,  $r_s$  and  $\rho$  will be smaller for the more compensated one. It seems apparent, however, that this would overestimate the conductivity in highly compensated samples because it neglects the repulsive effect of the additional charged minority impurities.

Crude as it is, the theory does not do badly in predicting the magnitude of the impurity band resistivity. This must be ascertained rather indirectly since we are not given  $N_{\text{maj}}$  and  $N_{\min}$ , but only their difference. Even this difference, obtained from the room temperature Hall constant, is somewhat in doubt because of the uncertainty in  $\mu_H/\mu$ . In the calculations to be described  $\mu_H/\mu$  was taken as 2. The observed  $\rho$  at 4°K was used in (8), along with the  $|N_D - N_A|$  value, to obtain values for  $N_{\text{maj}}$  and  $N_{\min}$ . The results for their ratio are shown in Table II for some of Fritzsche's samples. In the last column of Table II are shown the values calculated by Fritzsche from the temperature dependence of mobility and Hall constant in the temperature range where the carriers are in the conduction band. Since, as stated by Fritzsche, the values of the last column can only be considered as giving order of magnitude, the agreement between the two sets of values looks reasonably good.

Although the theory does well in the respects described, the temperature dependence predicted by (7) is incorrect. It has been found experimentally<sup>4</sup> that  $\sigma$  in the lowest temperature range is given by  $C_3 e^{-E_3/kT}$  for Ga-, In-, and Sb-doped samples. A possible origin for such temperature dependence is in the conduction

process involving an excited state or band which is higher in energy by  $E_3$  than the ground state. Although there is some variation of  $E_3$  with concentration (attributable, on this mechanism, to narrowing of the band gaps with increasing concentration) its value is approximately  $10^{-3}$  ev. In the case of Sb-doped Ge there is evidence for an excited state or band this close to the ground state.<sup>37</sup> The extent of the electron wave function in this state should be somewhat larger than that in the ground state. An electron excited into this state could therefore have a considerably larger jump frequency than one in the ground state. Conduction through this excited state should lead to the  $\rho$  of (7) modified in only two respects: (1) the replacement of  $\Delta E$  by the value appropriate to this state, presumably larger, (2) multiplication by a factor  $e^{-E_3/kT}$  times the ratio of the statistical weights of the two states. Thus with this mechanism one would retain the desirable feature of being able to explain the dependence of  $\rho$ , or more specifically  $C_3$ , on majority and minority impurity concentration. There is one major difficulty with this mechanism, however: it does not seem applicable to any case but that of Sb-doped material. There is no reason to believe that there is an excited state so close to the ground state in Ga- or In-doped Ge. A careful investigation of excited states of acceptors, similar to that carried out for donors, has, however, not yet been published.

It might be mentioned that it is very unlikely that this excited band is the one corresponding in position (more or less) to the hydrogenic  $n=2$  band. If this extended down so far it would be a fairly wide band, overlapping the conduction band, and it would then be difficult to explain the strong dependence of  $C_3$  on impurity concentration. On just this basis, in fact, one might speculate that the term  $C_2 e^{-E/kT}$  found by Fritzsche<sup>4</sup> in the  $\sigma$  of some Ga-doped samples represents conduction in an  $n=2$  band. It is not unreasonable that, in the concentration range for which this term appears in  $\sigma$ , the  $n=2$  band is both wide enough to support this type of conduction and more or less separated from other bands. Further, the existence of a fairly well defined group of electrons with mobility different from those of the conduction band and lower impurity bands might also account for the additional hump observed in the Hall curves of the samples which show this term in  $\sigma$ . It is apparent that to test this hypothesis and others more must be known about excited bands and their behavior with changing impurity concentration.

We conclude that, although one must have reservations about the crude theory of the last section, it does indicate that prospects are good for accounting for impurity band conduction down to about  $10^{15}/\text{cm}^3$  in germanium and perhaps lower in more highly compensated samples than those discussed here. In the

<sup>36</sup> L. C. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 327.

<sup>37</sup> E. M. Conwell, Phys. Rev. **99**, 1195 (1955).

case of silicon, the lowest concentration for which signs of impurity band conduction of the type discussed in part II have been observed is about  $10^{17}/\text{cm}^3$ . This is not far below the concentration listed in the last column of Table I, and the germanium results suggest that it will not be difficult to account for this.

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## Galvanomagnetic Theory for Electrons in Germanium and Silicon: Magnetoresistance in the High-Field Saturation Limit\*

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For constant scattering time  $\tau$  and ellipsoidal energy surfaces, the Boltzmann transport equation reduces to a phenomenological equation of motion for electrons from which a conductivity tensor is derived. The calculations for germanium and silicon differ in the orientation of the ellipsoids. The resistivity tensor is evaluated in the saturation limit, and explicit expressions for the angular dependence of the magnetoresistance are elaborated for certain high-symmetry combinations. The theoretical findings are in qualitative agreement with experiment, thus providing confirmation of the 4- or 8-ellipsoid [111] and the 3- or 6-ellipsoid [100] models of the energy surfaces in  $n$  germanium and  $n$  silicon, respectively. Essential agreement with energy-dependent  $\tau$  theory is also established.

## INTRODUCTION

**I**NDEPENDENT reports by Abeles and Meiboom<sup>1</sup> and by Shibuya<sup>2</sup> have demonstrated that the galvanomagnetic behavior of  $n$  germanium is successfully accounted for by the application of Boltzmann transport theory using the model of eight ellipsoidal energy surfaces located along the [111] axis in the Brillouin zone. Their analyses were formulated in terms of an energy-dependent scattering time  $\tau$  which, in particular, represented lattice scattering.

This paper describes a different approach to the problem which was a natural outgrowth of the theoretical interpretation of the cyclotron resonance experiments of Lax, Zeiger, and Dexter<sup>3</sup> in which a constant  $\tau$  was found adequate. It was thought that a constant- $\tau$  theory might adequately describe the observations of Pearson and Suhl,<sup>4</sup> although such a restrictive assumption is not truly justified over all temperatures. The advantage of this approach is that the Boltzmann theory reduces to a relatively simple phenomenological description. We also by-pass the difficulties involved in carrying through a precise treatment of the scattering processes. It is known that there are uncertainties in the temperature variation of the mass ratio  $K$ , the

validity of neglecting intervalley and interband scattering,<sup>5</sup> and the anisotropy of  $\tau$ . Thus, one may not be much worse off in working with a constant  $\tau$ .

In this light, our theory, while not generally physically realistic, has the virtue of being the simplest possible approach. This is not to say that it is entirely rid of cumbersome algebra; but at least the results can be more clearly expressed and explicitly evaluated. While we will initially follow a course which is applicable over all ranges of magnetic field, we will specialize to the high-field saturation limit when taking the inverse of the conductivity tensor, and leave the more complicated intermediate field case for a separate report. This permits us to concentrate on the magnetoresistance in this paper, since for  $H \rightarrow \infty$  the Hall coefficient  $R_H$  is simply  $(nqc)^{-1}$ .

### PHENOMENOLOGICAL CALCULATION OF THE EFFECTIVE CONDUCTIVITY TENSOR FOR COMBINATIONS OF ELLIPSOIDAL ENERGY SURFACES

Use of the constant  $\tau$  in the Boltzmann transport equation leads to the phenomenological equation of motion first proposed by Shockley<sup>6</sup>:

$$[(\nu + j\omega)\mathbf{m} + q\mathbf{B} \times] \mathbf{v} = q\mathbf{E}, \quad \nu = 1/\tau. \quad (1)$$

The relation describes the forced, damped oscillation of an electron in a single ellipsoidal energy surface characterized by the mass tensor  $\mathbf{m}$ , which is given in

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<sup>2</sup> M. Shibuya, *Phys. Rev.* **95**, 1385 (1954).

<sup>3</sup> Lax, Zeiger, and Dexter, *Physica* **20**, 818 (1954).

<sup>4</sup> G. L. Pearson and H. Suhl, *Phys. Rev.* **83**, 768 (1951).

<sup>5</sup> C. Herring, *Bell System Tech. J.* **34**, 237 (1955).

<sup>6</sup> W. Shockley, *Phys. Rev.* **90**, 491 (1953).