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Electrical Properties of *N*-Type Germanium*

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Measurements of conductivity and Hall effect from 11°K to 300°K on a set of *n*-type germanium samples covering the range from intrinsic to degenerate are reported. The purity and uniformity of the samples and extensiveness of the data permit a more thorough-going comparison with theory than has been possible in previous work.

The theory of mobility is reviewed briefly. The treatment of impurity scattering by Brooks and Herring is presented, and their formula for the impurity mobility is used throughout. An analytical formula for obtaining the mobility from lattice and impurity mobilities is included. The effect of electron-electron collisions on the mobility is considered in a qualitative manner.

The principal conclusions concerning the mobility are as follows: (1) Over the range 20.4°K to 300°K the lattice mobility varies as $T^{-1.64}$ rather than the theoretically predicted $T^{-1.5}$. (2) The impurity mobility increases with temperature less rapidly than the theoretical formula predicts, the exponent of T in the numerator being apparently between 1.0 and 1.5. (3) The Erginsoy formula for neutral impurity scattering appears to fit the experimental data reasonably well for a value of effective mass about one-third the free electron mass. (4) Dislocation scattering is negligible, leading to the conclusion that the density of edge-type dislocations is less than $10^6/\text{cm}^2$.

In fitting the concentration data, the parameters involved are activation energy, acceptor concentration, and effective mass. An effective mass in the neighborhood of one-quarter the free electron mass gives the best fit for all samples. The values of acceptor concentration obtained in this way for this effective mass agree well with those calculated from the low-temperature mobility values. The activation energy obtained for the purer samples is 0.0125 ev, in agreement with the value calculated from the hydrogen-like model for one-quarter the free electron mass.

The variation of activation energy with concentration does not agree with that observed by Pearson and Bardeen for *p*-type silicon. The effects which have been proposed to explain the variation are: residual potential energy of attraction between free electrons and ionized donors, screening of trapping centers by the free electrons, polarization of neutral centers by free electrons. It is concluded that a combination of the three effects will probably be required to explain the results.

The ratio of Hall to drift mobility is shown to agree with the theoretically predicted value within about 10 percent in the range 78°K to 300°K.

I. INTRODUCTION

MEASUREMENTS of conductivity and Hall effect have been made on a new set of germanium samples with widely varying amounts of added arsenic in the temperature range from 11°K to 300°K. The room temperature resistivities of these samples varied from 43 ohm cm to 0.005 ohm cm. Special precautions were taken in the growing of the crystals to ensure uniformity of the impurity distribution and a minimum of impurities other than the arsenic. The fact that the Hall mobilities of these samples at 300°K are higher than any previously reported[1] is presumably evidence for the greater perfection of these crystals.

From the measurements carrier concentration and Hall mobility were computed, and the results so obtained compared with existing semiconductor theory. This theory is based on a number of simplifying assumptions, of which the major one is that of spherical surfaces of constant energy in the conduction band. There is now a considerable body of evidence, experimental and theoretical, that this is untrue. Magnetoresistance data for *n*-type germanium cannot be explained in terms of spherical energy surfaces.[2] Calculation of the band structure of germanium[3] yields the result that the edge of the conduction band is not at $k=0$, in which case the constant energy surfaces are not spherical.[4] It is nevertheless significant, and perhaps not surprising, that in many respects the simple theory gives quite good agreement with experiment.

A parameter which appears throughout in the theory is the effective mass. In practice the process of comparison of theory and experiment is frequently just that of determining a value of the effective mass in some particular context. Thus, deviations from the simple theory may show up as differences in the effective mass computed from different types of data, or from the same type of data at different temperatures.

In this article we first present the description of experimental techniques and experimental results. Mobility theory and analysis of the mobility data are in the two succeeding sections, and theory and analysis of the concentration data follow this.

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[1] Hall mobilities of these samples at 300°K have been reported by P. P. Debye and E. M. Conwell, Phys. Rev. **87**, 1131 (1952).

[2] G. L. Pearson and H. Suhl, Phys. Rev. **83**, 768 (1951). Although magnetoresistance data have not been taken for this new set of samples, it is unlikely that the results will be very different.

[3] F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953).

[4] These results might be incorrect to the extent that the edge of the conduction band is at $k=0$, or at the edge of the Brillouin zone. According to the calculations, however, at $k=0$ the conduction band is triply degenerate. Since it seems unlikely that these calculations would give the symmetry type incorrectly, it seems definite that wherever the edge of the conduction band the constant energy surfaces are nonspherical.

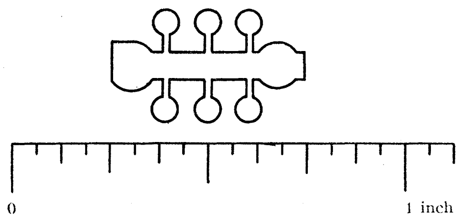

Fig. 1. Germanium sample.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The single crystals from which the samples were cut were grown from germanium which had been very carefully purified by either zone refining[5] or repeated crystallization with subsequent discarding of the crystal end containing most of the impurities. A few of the purer crystals were grown by zone leveling.[6] The remainder were pulled from the melt by the method reported by Teal.[7] In the case of the doped crystals a small amount of arsenic was added in the melt before the final crystal was grown.[8]

The germanium samples were prepared in the standard manner by cutting with a diamond wheel a slice of about 0.050 inch thickness perpendicular to the long axis of the single crystal.[9] This orientation was chosen because it gives the smallest over-all change in resistivity. This slice was lapped to a specified thickness (0.015–0.045 in.), and mounted on a glass plate with sealing wax. The desired "bridge" shape (Fig. 1) was then obtained by cutting away the unwanted portions of the germanium with a vibrating steel dye.[10] The large areas on both ends of the bridge were used for the current leads, the center arms for the Hall measurements and either pair of outside arms on the same side for resistivity measurements.[11] The ends for the current leads were made unequal for easy identification. Some of the advantages claimed for this configuration are that the actual contact areas are far removed from the area of measurement and that the unbalance voltage across the Hall arms due to the sample current is always practically zero.

The bridge was probed at 0.05-cm intervals along its center line to measure the room temperature resistivity and check uniformity. If there was any nonuniformity in the immediate Hall area, its resistivity was corrected accordingly.

The completed bridge was mounted in the sample holder. This consisted essentially of a hollow brass block at the inside of which the bridge was clamped into place. The large mass of the holder (about 300 g) served to give good temperature stability. The brass block also contained the platinum resistance thermometer and a small heater. The block was suspended on thin (0.004-in. wall) Monel tubing which also supported two radiation shields. All lead wires ran inside this tube. The complete assembly was enclosed by a glass Dewar 18 in. long, which was surrounded by a vacuum-tight brass casing. By connecting a vacuum pump to the Dewar, it was possible to reduce the pressure over the refrigerant and, therefore, the temperature of its boiling point. With liquid hydrogen as the refrigerant, this arrangement gave a minimum temperature of about 10.8° Kelvin.

The temperature range of the measurements usually extends from about 11° to somewhat above 300° Kelvin. At the boiling points of nitrogen and hydrogen and below the latter the sample was substantially in temperature equilibrium with the holder and thermometer. For the regions from 20.4° to 78° and 78° to

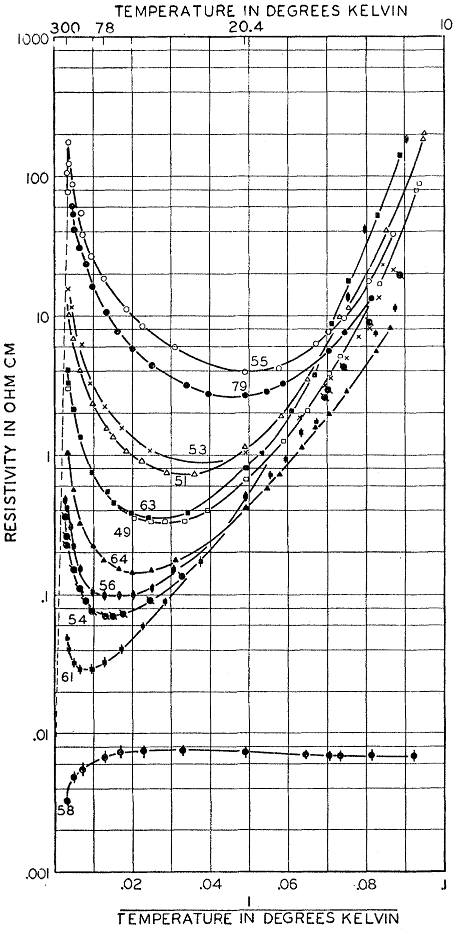

Fig. 2. Resistivity of a set of n-type germanium samples (arsenic-doped) as a function of inverse absolute temperature.

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[5] W. G. Pfann, J. Metals 4, 747 (1952); W. G. Pfann and K. M. Olsen, Phys. Rev. **89**, 322 (1953).

[6] The zone-melted materials were supplied by W. G. Pfann and K. M. Olsen of Bell Laboratories.

[7] G. K. Teal and J. B. Little, Phys. Rev. **78**, 647 (1950).

[8] The pulled crystals were supplied by E. Buehler and W. W. Bradley of Bell Laboratories.

[9] Much of the sample preparation work, to be described in the succeeding paragraphs, was carried out by J. P. Maita of Bell Laboratories who also made many contributions to the techniques used.

[10] This is described by W. L. Bond, Phys. Rev. **78**, 646 (1950).

[11] Germanium samples of this shape had been used previously for Hall and resistivity measurements by G. L. Pearson of Bell Laboratories.

300° Kelvin, where the sample holder was allowed to warm up slowly in vacuum, it was shown that the temperature differential between sample and thermometer was also insignificant. The resistance of the platinum thermometer was measured with a Mueller bridge, and then converted into temperature according to a calibration made by the National Bureau of Standards.

The field strength of the electromagnet (gap $2\frac{1}{8}$ in.) was measured by comparison with a secondary standard which had also been calibrated at the National Bureau of Standards. The Hall effect was measured with fields of up to about 4000 gauss, the field being always low enough to stay within the linear range. The dc measurements were made with a type $K2$ potentiometer and galvanometer. The sample current was measured with a vacuum-tube microammeter. All the wiring and batteries with the exception of the potentiometer were shielded.

The resistivities of eleven samples as a function of the inverse absolute temperature are shown in Fig. 2. The intrinsic behavior is indicated by a dashed line. For relatively pure materials the resistivity goes through a broad minimum when the temperature is lowered and reaches in the range 10°–13°K values which are comparable to those at room temperature. When more impurities are introduced, the resistivity minimum moves to higher temperatures and its values in the 10°–13°K range lie appreciably above those at ambient temperatures. Finally, sample 58, which contains enough impurities to make it degenerate over most of the temperature range, shows almost no change in resistivity with temperature.

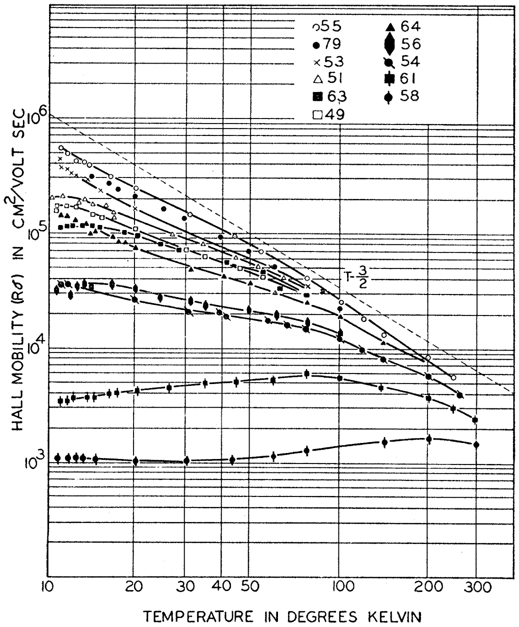

FIG. 4. Hall mobility of a set of n-type germanium samples (arsenic-doped) as a function of absolute temperature.

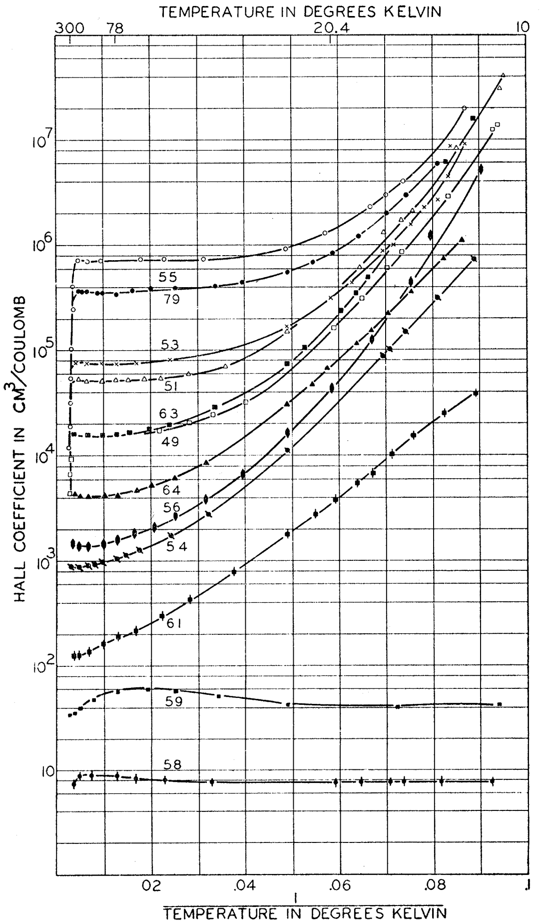

FIG. 3. Hall coefficient of a set of n-type germanium samples (arsenic-doped) as a function of inverse absolute temperature.

The Hall coefficient R in cm³/coulomb was obtained from the equation[12]

$$R = tV\times10^8/HI, \qquad (1)$$

and is plotted as a function of the inverse absolute temperature in Fig. 3. In this equation t represents the thickness of the bridge in cm, V is one-half the sum of the Hall voltages in volts measured with the magnetic field in the normal and in the reversed direction, and I is the current in amperes. While most of the samples in their low-temperature behavior fall into a more or less consistent pattern, samples 56 and 63 show a much larger slope than their neighbors. Both these samples had been cut from near the tip end of the crystal and therefore probably contained a larger total impurity concentration.

Resistivity and Hall data were combined to give Hall mobility, defined as R/ρ. This is plotted as a function of temperature in Fig. 4. From the definition of Hall mobility it follows that electron concentration n is

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[12] See, for example, W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 213.

given by

$$n = \frac{\mu_H}{\mu} \frac{1}{Re} \tag{2}$$

for extrinsic samples. The ratio μ_H/μ is a function of impurity concentration and temperature, but does not differ greatly from unity.[13] It is customary to neglect this factor and consider $1/Re$ equal to n. Figure 10 contains plots of $1/Re$ as a function of temperature for some of the samples. The effect of neglecting the difference between μ_H/μ and 1 is small, as will be shown later.

III. MOBILITY THEORY

There are four types of scattering process which have been studied theoretically for semiconductors: lattice, ionized impurity, neutral impurity, and dislocation. In this section these will be discussed in that order for the case where the electrons obey Maxwell-Boltzmann statistics. There are not sufficient data on degenerate samples to warrant considering that case in detail. Some qualitative considerations concerning the effect of electron-electron collisions on the mobilities so obtained will also be presented. The following notation will be used:

σ = conductivity (ohm^{-1} cm^{-1})
R = Hall coefficient
μ = mobility (cm^2/volt sec)
$\mu_H = R\sigma$ = Hall mobility (cm^2/volt sec)
μ_L = lattice mobility (cm^2/volt sec)
μ_I = ionized impurity mobility (cm^2/volt sec)
μ_N = neutral impurity mobility (cm^2/volt sec)
μ_D = dislocation mobility (cm^2/volt sec)
n = density of conduction electrons (/cm^3)
N_D = density of donors (/cm^3)
N_A = density of acceptors (/cm^3)
N_I = density of ionized impurities (/cm^3)
N_N = density of neutral impurities (/cm^3)
e = magnitude of charge on the electron = 1.60×10^{-19} coulombs
m = mass of the electron in free space = 9.03×10^{-28} g
m_n = effective mass of a conduction electron (g)
k = Boltzmann's constant = 1.37×10^{-16} erg/degree
T = absolute temperature (°K)
$\hbar$ = Planck's constant/2π = 1.04×10^{-27} erg sec
$\mathcal{E}$ = kinetic energy (ergs)
τ = relaxation time (sec)
κ = dielectric constant, 16.1 for germanium
l_L = mean free path for lattice scattering (cm)
c_{ll} = average longitudinal elastic constant
$\mathcal{E}_{1n}$ = shift of edge of conduction band per unit dilation (ev)
$\mathcal{E}_{1p}$ = shift of edge of filled band per unit dilation (ev)

3.1 Lattice Scattering

Several theoretical treatments of scattering by lattice vibrations have been carried out[14] with essentially equivalent results. In the Bardeen-Shockley derivation the lattice mobility is given by

$$\mu_L = \frac{(8\pi)^{\frac{1}{2}} \hbar^4 c_{ll}}{3 \mathcal{E}_{1n}{}^2 m_n{}^{5/2} (kT)^{\frac{3}{2}}}. \tag{3}$$

It is usually considered that the temperature variation of $\mathcal{E}_{1n}$, m_n, and c_{ll} can be neglected. This has been substantiated for the last of these three in the case of germanium. It has been found experimentally that in the temperature range from 78°K to 293°K the elastic constants of germanium decrease about 3 percent,[15] which is negligible for the present purposes. The lattice mobility should then vary with temperature as $T^{-\frac{3}{2}}$. It should be mentioned, however, that underlying the $\frac{3}{2}$-power dependence is the assumption that the band edge is located at the center of the Brillouin zone. For the band edge at $k=0$ the electron interacts with low-energy lattice quanta, for which equipartition is satisfied, and this leads to a matrix element for the transition independent of electron speed and proportional to T. If the band edge is not at the center of the zone, as the band structure calculation indicates, this may not be the case.

3.2 Ionized Impurity Scattering

Scattering by ionized impurities was first treated in somewhat crude, essentially classical fashion. Each ion was considered to scatter independently of all the others, with its scattering x section arbitrarily cut off at a distance equal to half the average distance between neighboring impurities. The latter assumption is partly justified by the screening of the impurities by the conduction electrons. Also, the neglect of scattering by more distant ions is to some extent compensated for by taking the deflection produced by a given ion as that which would be gotten if the electron traversed an infinite path in the presence of the ion. A derivation incorporating these features leads to the impurity scattering formula which has been widely used,[16]

$$\mu_I = \frac{2^{7/2}}{\pi^{\frac{3}{2}}} \frac{\kappa^2 (kT)^{\frac{3}{2}}}{m_n{}^{\frac{1}{2}} e^3 N_I} \frac{1}{\ln[1 + (3\kappa kT/e^2 N_I{}^{\frac{1}{3}})^2]}. \tag{4}$$

A quantum-mechanical treatment has been carried out by Brooks[17] and independently by Herring.[18] This involves a collective treatment of the ion scattering.

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[13] See Eq. (17) and accompanying text.

[14] A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1936); A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Julius Springer, Berlin, 1933), Vol. 24, Part 1; F. Seitz, Phys. Rev. **73**, 549 (1948); J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

[15] H. J. McSkimin (private communication).

[16] E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).

[17] H. Brooks, Phys. Rev. **83**, 879 (1951).

[18] C. Herring (private communication).

The potential due to each ion is taken as a screened Coulomb potential. A Fourier analysis of the potential due to a random distribution of screened ions is carried out, and the results used in computing the matrix elements of the perturbing potential. This leads to a mobility which differs from (4) only in the replacement of the logarithmic term, e.g.,[18]

$$\mu_I=\frac{2^{7/2}}{\pi^{\frac{3}{2}}}\frac{\kappa^2(kT)^{\frac{3}{2}}}{m_n{}^{\frac{1}{2}}e^3N_I}\frac{1}{\ln(1+b)-b/(1+b)}, \tag{5}$$

where

$$b=\frac{6}{\pi}\frac{\kappa m_n k^2T^2}{n\hbar^2e^2}. \tag{6}$$

For $n=N_I$, the two formulas give closely the same results; this is shown in Fig. 5, where the two mobilities are plotted as a function of impurity concentration at 300°K and 78°K. For this plot the effective mass has been taken as one-quarter the free-electron mass.[19] The two formulas give quite different results, however, when the conduction electron density is appreciably less than the ionized impurity density, the Brooks-Herring formula giving a lower mobility for the same concentration of ionized impurities. It has been pointed out by Herring that this is essentially due to the fact that (5) takes into account the decrease in screening when n is less than N_I while (4) does not. With less effective screening the same ionized impurity concentration will of course scatter more effectively, giving smaller electron mobilities.

A derivation of the ionized impurity scattering which takes into account the contribution of the dilatation of the lattice around the impurity ion has also been carried out.[20] This leads to the previous formula with the logarithmic term replaced by a complicated integral which must be evaluated numerically. Since the effect concerned is probably small this formula was not used in the comparison with the experimental data.

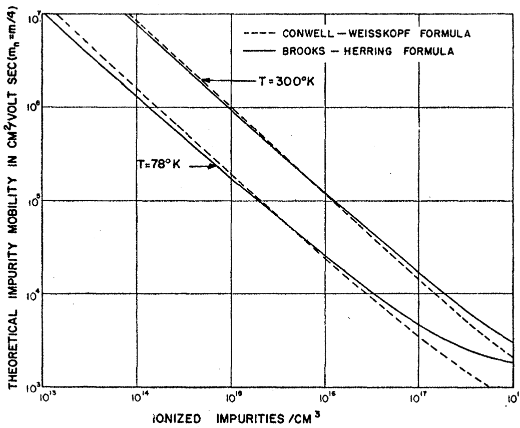

FIG. 5. Plots of impurity mobility *vs* ionized impurity concentration from Conwell-Weisskopf and Brooks-Herring impurity scattering formulas at 78°K and 300°K.

3.3 Neutral Impurity Scattering

Because of the analogy between a neutral donor or acceptor and a hydrogen atom, the mobility for scattering by neutral donors or acceptors can be obtained by suitable modification of the results for scattering of slow electrons by hydrogen. This has been carried out by Erginsoy,[21] leading to

$$\mu_n=\frac{1}{20}\frac{m_ne^3}{N_N\kappa\hbar^3}. \tag{7}$$

The density of neutral impurities can, of course, be obtained directly from the Hall data.

3.4 Dislocation Scattering

The scattering of dislocations due to the lattice dilatation they produce has been calculated theoretically by Dexter and Seitz.[22] This gives a mobility which is proportional to T and inversely proportional to the number of dislocation lines per cm², which of course is unknown. For what would appear to be a reasonable dislocation density in germanium this process would only be of importance at low temperatures. There it would be difficult to separate from the ionized impurity scattering since the density of acceptors, which are all ionized, is unknown. Neglect of the dislocation scattering is more adequately justified, however, by the fact that it appears quite possible to account for the observed mobilities over the entire temperature range by the action of the scattering mechanisms previously cited. In sample 55, for example, the acceptor concentration required to account for the mobility observed at 11.5° is about $10^{12}/\text{cm}^3$ if it is assumed that only lattice and impurity scattering are operative. Since this is already quite small it is unlikely that there is appreciable dislocation scattering in this sample. From this it can be concluded, with the use of the Dexter-Seitz formula, that the dislocation density in this sample is less than $10^6/\text{cm}^2$.[23] Since there appears no reason why dislocation density should increase with impurity concentration, this estimate should be valid for all these samples.

3.5 Effect of Electron-Electron Collisions

In the previously mentioned derivations of mobility only the interaction of the electrons with the particular scattering mechanism was considered. The interaction of the electrons with each other may, however, prevent these mobilities from being realized.[24] The effect can be

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[19] Evidence for this effective mass has been presented by P. P. Debye and E. M. Conwell, reference 1. Further evidence will be considered in the course of the present paper.

[20] C. Horie, Sci. Repts. Tôhoku Univ. **34**, 29 (1950).

[21] C. Erginsoy, Phys. Rev. **79**, 1013 (1950).

[22] D. L. Dexter and F. Seitz, Phys. Rev. **86**, 964 (1952).

[23] This estimate is based on an effective mass of $m/4$ with $\mathcal{E}_{1n}$ corrected accordingly. See Sec. 4.1.

[24] To the authors' knowledge this was first demonstrated for the case of ion scattering, by Cohen, Spitzer, and Routly, Phys. Rev. **80**, 230 (1950).

understood as follows. The current density for a given value of electric field intensity depends on the total electron momentum developed by the field. This in turn depends on the rate of momentum transfer to the scattering mechanism. Electron-electron collisions do not affect the current density directly since they cannot alter the total momentum. They do, however, tend to randomize the way in which this total is distributed among the different velocity groups. When the scattering mechanism is such as to lead to a nonuniform distribution, electron-electron collisions will give rise to a net transfer of momentum from electrons which dissipate it less efficiently to those which dissipate it more efficiently, resulting in an over-all greater rate of momentum transfer and lower mobility. Conversely, if the scattering mechanism is such as to lead to a uniform distribution, electron-electron collisions will not, as in the previous case, provide a more efficient mechanism for momentum transfer to the scatterers, and the mobility will be unaffected.

On the basis of this discussion it is apparent that the size of the effect of electron-electron collisions on the mobility is a function of the velocity dependence of the relaxation time. Thus, in particular, for neutral impurity scattering where the relaxation time is not a function of velocity, the mobility will not be affected by electron-electron collisions. Also, ion scattering should be much more affected than lattice scattering since in the former case τ is proportional to v^3, while in the latter it is proportional to v^{-1}.

It has been pointed out by Herring that it is possible to compute simply an upper limit for the size of this effect under the usual simplifying assumptions about the band structure. If the electron-electron collisions were completely effective in randomizing the drift velocities, the electron distribution in an electric field would be a Maxwell-Boltzmann distribution centered about $v=v_d$, the drift velocity. It can then be calculated that the maximum effect of these collisions would be to multiply μ_I by a factor 0.3, μ_L by 0.88. A calculation of the effect on μ_I has been carried out classically and leads to a factor 0.6.[25] This should be reasonably accurate for low electron densities and high temperatures. No calculation has been made for the case of lattice scattering. It is reasonable to expect here a factor of perhaps 0.95 for low electron densities. With increasing electron density this should decrease toward the limiting value 0.88 because of the increased frequency of electron-electron collisions compared to the electron-lattice collisions.

3.6 Combination of Mobilities

For a Maxwell-Boltzmann distribution of the electron energies and spherical surfaces of constant energy it can be shown[26] that the mobility, with electron-electron interaction neglected, depends on the relaxation time,

$$\mu=\frac{e}{m_n}\frac{\langle v^2\tau\rangle}{\langle v^2\rangle}. \tag{8}$$

If dislocation scattering is neglected the relaxation time can be written

$$\frac{1}{\tau}=\frac{1}{\tau_L}+\frac{1}{\tau_I}+\frac{1}{\tau_N}. \tag{9}$$

We shall consider first the case in which neutral impurity scattering can also be neglected. If we introduce the notation

$$v_T=(2kT/m_n)^{\frac{1}{2}}, \tag{10}$$

$$x=v^2/v_T^2=\mathcal{E}/kT, \tag{11}$$

the relaxation times can be written

$$\tau_L=l_L/v_Tx^{\frac{1}{2}}, \tag{12}$$

$$\tau_I=B(x)v_T^3x^{\frac{3}{2}}, \tag{13}$$

where $B(x)$ is a slowly varying function of x. Substitution of these expressions for the relaxation times in (8) leads to

$$\mu=\mu_L\int_0^\infty\frac{x^3e^{-x}}{(l_L/B(x)v_T^4)+x^2}dx. \tag{14}$$

Since $B(x)$ varies slowly with x it would be quite satisfactory to replace it in this integral by a constant which is its value at the maximum of the integrand. This is what is done in the evaluation of μ_I from (8). In that case the maximum of the integrand occurs at $x=3$. It can then be shown that

$$l_L/B(3)v_T^4=6\mu_L/\mu_I. \tag{15}$$

Since the maximum of the integrand of (14) is not easy to determine, in past derivations,[27] the term $l_L/B(x)v_T^4$ has been replaced by $6\mu_L/\mu_I$ or $B(x)$ replaced by $B(3)$. Although the error due to the use of this approximation is not negligible, it has the great advantage that it permits the evaluation of the integral in closed form,[28] e.g.,

$$\mu=\mu_L[1+q^2\{\mathrm{Ci}q\cos q+\mathrm{Si}q\sin q-\tfrac{1}{2}\pi\sin q\}], \tag{16}$$

where

$$q^2=6\mu_L/\mu_I.$$

Since these functions are all tabulated, calculation of μ from this formula involves little more effort than calculation from the more usual approximation employing the sum of the reciprocals.[29]

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[25] L. Spitzer, Jr., and R. Härm, Phys. Rev. **89**, 977 (1953).

[26] Reference 12, p. 276.

[27] H. Jones, Phys. Rev. **81**, 149 (1951) and V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **82**, 977 (1951).

[28] This was pointed out by H. Jones, reference 27.

[29] A graph of μ/μ_L as a function of μ_L/μ_I, computed from (16) has been published by E. Conwell, Proc. Inst. Radio Engrs. **40**, 1331 (1952). Percent difference between the mobilities computed from (14) and from the sum of the reciprocals, which may be quite appreciable, is plotted by V. A. Johnson and K. Lark-Horovitz, reference 27.

It can be seen that the approximation (16) will always lead to too small values of μ for a given μ_L and μ_I. The electrons which make the maximum contribution to μ_I are relatively fast ones. It has already been stated that they have energy of about $3kT$. These are just the ones, however, which are more effectively scattered by the lattice vibrations. When both scattering mechanisms are operative, therefore, the group of electrons which makes the maximum contribution to the mobility will certainly have energy less than $3kT$. The maximum of the integrand of (14) will, therefore, always occur at smaller values of x than $x=3$. Since B is a monotonically decreasing function of x the mobility calculated using $B(3)$ will, as previously stated, always be too small. The error will clearly be negligible, however, if $\mu_L \gg \mu_I$ or $\mu_L \ll \mu_I$.

Numerical integration of (14) was carried out for a number of cases to determine the magnitude of the error. For μ_I taken from (4), at 78°K the error was found to be about 9 percent at $N_I=10^{15}$ ($\rho \simeq 0.3$ ohm cm), 13 percent at $N_I=10^{17}$ ($\rho \simeq 0.01$ ohm cm), while for μ_I from (5), at this temperature it was 3 percent at 10^{15}, 6 percent at 10^{17}. It is to be expected that the error would be smaller in the latter case; the logarithmic term of (4) contains x to the second power, while that of (5) is linear in x. If, as was done in the calculations, values of μ computed from (16) are used to compute ρ for comparison with the experimental μ *vs* ρ the error is, of course, magnified. As will be seen later, it does affect somewhat the conclusions which can be drawn about effective mass from comparison of experiment and theory. These are also affected somewhat by electron-electron collisions, as will be demonstrated in a later section.

For comparison with experimental data it is necessary to compute the Hall mobility $R\sigma$, rather than μ. It can be shown that for a Maxwell-Boltzmann distribution and spherical energy surfaces the ratio of μ_H to μ is given by[30]

$$\frac{\mu_H}{\mu}=\frac{\langle v^2\tau^2\rangle}{\langle v^2\rangle}\div\left(\frac{\langle v^2\tau\rangle}{\langle v^2\rangle}\right)^2. \tag{17}$$

This ratio has been calculated as a function of μ/μ_I by Jones[31] and by Johnson and Lark-Horovitz,[32] for the case in which neutral impurity scattering is negligible, with the same approximation of replacing $B(x)$ by $B(3)$. The error due to this is no more than a few percent, however, for small μ_L/μ_I which turns out to be the only range in which the precision of this correction is important for comparison with these experimental data.

We consider now the effect of electron-electron collisions. As previously indicated, this will multiply the mobility by a factor, to be denoted by γ which is less than 1. The size of this factor depends on the relative frequency of collisions of electrons with each other and with the scatterers, and on the relative importance of lattice and impurity scattering, or μ_L/μ_I. It is possible to make some qualitative predictions about the effect of the latter which are useful. To this end consider the variation of relaxation time with μ_L/μ_I. For $\mu_L/\mu_I=0$, τ is proportional to $1/v$ and slow electrons develop much greater drift velocities than fast ones. The initial effect of increasing μ_L/μ_I is to reduce this asymmetry, i.e., make τ less velocity-dependent, because ionized impurities scatter slow electrons much more strongly than fast ones. It is in general at least a fair approximation to represent τ as a constant$\times v^n$, where n is, of course, a function of μ_L/μ_I. In this range, n would vary from -1 to 0. As μ_L/μ_I increases beyond this, impurity scattering begins to dominate. Fast electrons then develop greater drift velocities than slow ones, this asymmetry becoming more marked as μ_L/μ_I grows. In this range the values of n are positive, increasing from 0 to 3, the latter obtained at $\mu_L/\mu_I=\infty$. This variation of the velocity dependence of the relaxation time is substantiated by the variation with μ_L/μ_I of μ_H/μ, which according to (17) is the weighted average of τ^2 divided by the square of the weighted average of τ. This ratio is 1.18 for $\mu_L/\mu_I=0$, decreases initially with μ_L/μ_I reaching a minimum of 1.03 around $\mu_H/\mu=0.1$, and then increases until it reaches 1.93 at $\mu_L/\mu_I=\infty$.

From what has been said previously, it can be seen that as μ_L/μ_I starts to increase from 0, γ can either increase or decrease, depending on whether the decreasing velocity dependence or the increasing frequency of electron-electron collisions is the more important effect. In either case, the change in γ up to $\mu_L/\mu_I=0.1$ should not be more than a few percent. Around $\mu_L/\mu_I=0.1$, γ can have a value at most a few percent higher than its value at $\mu_L/\mu_I=0$. Beyond 0.1, γ will decrease consistently, and more rapidly, as μ_L/μ_I increases. It will not get as small as 0.6, however, because the degenerate region will be reached before impurity scattering dominates the situation to this extent. When Maxwell-Boltzmann statistics cease to be valid the interaction of electrons with ones of different velocity groups is limited by the Pauli principle and electron-electron collisions decrease in importance.

In the case in which neutral impurity scattering is also important, calculation of the mobility to the accuracy of (16) would involve considerably more numerical effort. Under the circumstances, it was considered that a sufficiently good approximation could be obtained by computing μ from

$$1/\mu=(1/\mu_{LI})+(1/\mu_N), \tag{18}$$

where μ_{LI} is the mobility computed from μ_L and μ_I according to (16). A sum of reciprocals should yield a considerably better approximation in this case than it does for the combination of μ_L and μ_I. In that case the electrons which boost the value of μ_I are discriminated

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[30] See reference 12, p. 277.

[31] H. Jones, reference 27.

[32] V. A. Johnson and K. Lark-Horovitz, reference 27.

against by the lattice scattering, those which boost μ_L are discriminated against by the impurity scattering, and neither group will make the contribution to the mobility implied by the values of the separate μ's. The neutral impurity scattering, however, is not velocity-dependent and does not therefore discriminate against any particular velocity group.

The presence of an appreciable amount of neutral impurity scattering will also affect the values of μ_H/μ and γ. Again, the effort involved in making any quantitative calculations here was not considered justified. It is apparent, however, that the presence of neutral impurity scattering will make τ less velocity dependent and thus in general decrease μ_H/μ and increase γ. In the limit of all neutral impurity scattering, both μ_H/μ and γ equal 1.

IV. ANALYSIS OF MOBILITY DATA

Before undertaking a detailed analysis of the mobility data we shall consider briefly some of the gross features of the variation with impurity content and temperature. The mobilities, as expected, decrease with increasing carrier concentration until very low temperatures, where the residual impurity concentration is large enough to take over in some cases. The temperature variation of the Hall mobility for these samples shows the wide range of behavior characteristic of the wide range of impurity concentrations. Sample 55 is so pure the mobility scarcely departs from the negative slope characteristic of lattice mobility down to the lowest temperatures observed. With increasing impurity concentration this departure appears at higher temperatures due to the greater importance of ionized impurity scattering relative to lattice scattering. It can be observed, however, that in most of the samples at temperatures below that for which the initial flattening of the slope appears, the slope again gets steeper, giving μ_H *vs* T an s shape. This is displayed well by sample 64, for example. Apparently the effect of impurity scattering is decreasing even though the temperature is decreasing. This can be explained by the fact that the ionized impurity content of these samples is decreasing as the temperature decreases due to electrons dropping back into donor centers. It indicates that N_A is much smaller than the saturation value of N_D-N_A, which is borne out by later calculations. Sample 61 is sufficiently impure to show a positive slope over a long temperature range. The fact that this never becomes as steep as predicted for ionized impurity scattering, however, suggests that this sample has large neutral impurity scattering as well. Sample 58 exhibits the approximately constant mobility characteristic of a degenerate sample.

For more quantitative comparison of experiment and theory the data are usefully broken down into the following parts:

1. Data for the range of temperatures and impurity concentrations for which impurity scattering is negligible. These afford a check on the theory of lattice scattering, mainly on the theoretically predicted temperature dependence since μ_L involves two unknown parameters m_n and $\mathcal{E}_{1n}$.
2. Data for the range of temperatures, 300°K to 78°K roughly, for which N_I is known and neutral impurity scattering is small or negligible; from these it is possible to obtain a check of much of the foregoing theory, and in particular of that for ionized impurity scattering.
3. Data for the temperature range below 78°; a rough check of the theory, now including neutral impurity scattering, can be obtained. The theory can be used to compute an approximate density of acceptors in the individual samples.

The three parts will be considered in that order.

4.1 Lattice Scattering Range

For the purer samples in the temperature range from about 78°K to where the samples become intrinsic it is seen that μ_H decreases more steeply than $T^{-1.5}$, going as $T^{-1.66}$ for the purest sample, approximately as $T^{-1.6}$ for the next several samples in order of purity. Since impurity scattering would only make the mobility go less steeply than $T^{-1.5}$, this section of the data must represent lattice mobility. In that case the theory of the preceding section predicts that μ_H/μ will be a constant, 1.18, over the temperature range concerned for these samples. It would then follow that the lattice mobility varies with temperature essentially as $T^{-1.6}$.

New drift mobility measurements on high-resistivity samples in the range 150°K to 300°K do indicate that μ_H/μ is constant and approximately equal to 1.1 in this range.[33] The difference between this value and 1.18 is within the limits of experimental error. Additional support for theory is provided by the carrier concentration data. In the range 78° to 300° $1/Re$ is essentially constant for the purer samples. Since $n=(\mu_H/\mu)\cdot(1/Re)$ and should furthermore be constant to within a few percent in this range, μ_H/μ must remain constant to within a few percent down to 78°K.

It follows that the observed temperature dependence is essentially that of μ_L and that the latter can reasonably be computed from the Hall mobility taking $\mu_H/\mu=1.18$. The values of μ_L which gave the best fit to the experimental data at a number of temperatures are shown in Fig. 6. A 20.4° value is included although this is in somewhat more doubt than the others since a correction had to be made for impurity scattering. From this plot μ_L varies with temperature as $T^{-1.64}$. As stated previously, this may result from the edge of the conduction band not being located at $k=0$.

It is interesting to note that effective masses of $m/4$ for electrons and holes in the deformation potential formulas for μ_L give about as good agreement with experiment for germanium as m. The values of $\mathcal{E}_{1n}$ and $\mathcal{E}_{1p}$ computed from (3) using the known room temperature mobilities of electrons and holes and effective

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[33] M. Prince (private communication).

masses of $m/4$ are 9.4 and 13.6 ev, respectively. The difference of these agrees reasonably well with the experimentally determined shift of the energy gap per unit dilation.[34]

4.2 78°K to 300°K Range

We consider now the temperature range 78° to 300°. For these samples the acceptor concentration is sufficiently small that in this range, where ionization of donors is practically complete, the density of ionized impurities can be taken equal to the density of conduction electrons. Also, neutral impurity scattering can be neglected in all but a couple of instances. Mobility is then a unique function of resistivity which can be calculated theoretically and compared with experimental values at any given temperature. This makes it unnecessary to compute for the individual samples, which is quite advantageous in view of the scatter of experimental results.

For the theoretical calculation μ_L was taken from the fit for the purest samples (see Fig. 6) and μ_I from the Brooks-Herring formula, Eq. (5). The mobility was then computed from the approximate formula (16). This was in turn used to compute ρ from $\rho = 1/ne\mu$. The mobility was converted to Hall mobility by use of (17), with the approximation discussed in the last section.

The values of μ_H/μ calculated from (17) were shown in the last section to be at least approximately correct for pure samples in this temperature range. By similar arguments this can be extended to less pure samples. Mobilities have been obtained at 300°K for resistivities ranging from 30 ohm cm to 0.05 ohm cm by drift mobility measurements.[33] These lead to a variation of μ_H/μ with resistivity or impurity concentration which is quite similar to that predicted by (17), but everywhere about 10 percent too low.[33] Again, it is felt that the discrepancy is within the limits of experimental error and use of μ_H/μ from (17) is justified.[35] An experimental determination of this kind is not available at temperatures below 300°K. For these temperatures, however, a demonstration of the approximate validity of (17) is provided by the concentration data. Consider the experimentally determined variation of $1/Re$ with temperature in the range 78° to 300° for moderately impure samples such as 64. Although carrier concentration should be constant or increasing slightly with temperature, $1/Re$ for such samples reaches a maximum below 300° and then decreases. μ_H/μ calculated from (17), however, is increasing with temperature in this neighborhood in just such a way as to give approximately constant or increasing n for these samples. Incorporation of μ_H/μ determined from the theoretical formula was therefore considered justified.

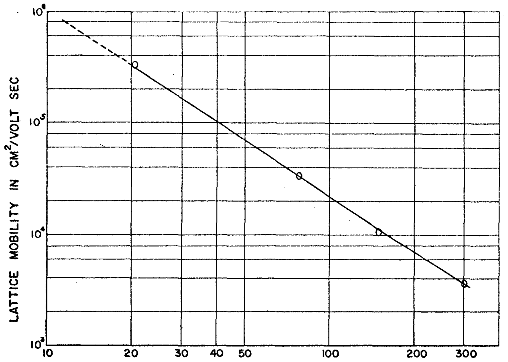

FIG. 6. Lattice mobility obtained from fits to the experimental data plotted *vs* absolute temperature.

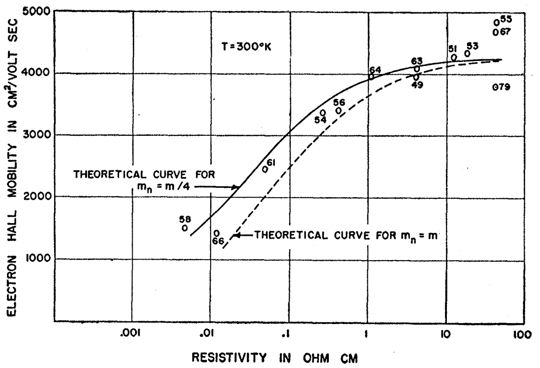

FIG. 7. Plots of experimental and theoretical Hall mobility *vs* resistivity at 300°K.

In the calculations described, the correction for electron-electron collisions is automatically included at the high resistivity end by choosing μ_L to fit the purest samples. This, however, applies to the whole curve some amount of correction. For the region up to and a little beyond the minimum of μ_H/μ the amount should be correct within a few percent. Right around the minimum the curve is possibly overcorrected and thus low by a few percent. Use of (16) will cause the theoretical curve to be low; this will amount to a few percent around the minimum of μ_H/μ.

Plots of the experimental data and theoretical curves for various values of m_n in (5) at temperatures of 300°, 150°, and 78° are shown in Figs. 7 through 9, respectively. The 300° situation will be considered first.[36] The minimum of the μ_H/μ curve occurs around 0.03 ohm cm, between samples 61 and 66. Because of the scatter of samples at this end of the resistivity scale it is difficult to apply the ideas of the preceding paragraphs

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[34] For a discussion of this subject see J. Bardeen and W. Shockley, reference 14.

[35] Drift measurements give directly the mobility of minority carriers in a sample. Conversion of this to majority carrier mobility introduces uncertainty because of the approximations involved.

[36] A similar pair of curves for 300° was published by P. P. Debye and E. M. Conwell, reference 1. They differ from those in Fig. 7, however, in that the impurity mobility was calculated from (4) in that case. The use of (5) raises the curve at the low-resistivity end (see Fig. 5), making the effective mass larger.

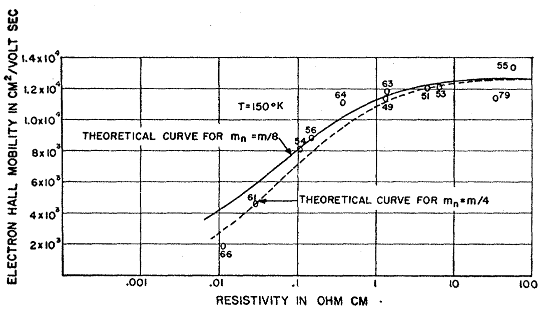

Fig. 8. Plots of experimental and theoretical Hall mobility *vs* resistivity at 150°K.

and to determine an effective mass. It does, however, seem reasonable to say that $m/4$ is a lower limit, with the best value lying between $m/4$ and $m/2$.

At 78° impurity scattering is beginning to affect even the purest samples, and better fits are obtained by using slightly different lattice mobilities with different effective masses. Determination of the effective mass at this temperature is complicated by the presence of neutral impurity scattering in the more heavily doped samples, e.g., 56, 54, 61. Since $1/Re$ at 78° is not much less than $1/Re$ at 300° for these samples, and the presence of neutral impurity scattering makes the published values of μ_H/μ inaccurate, the density of neutral impurities cannot be determined with any precision. It can nevertheless be shown that the correction to the mobility from this source should be of the order of 10 percent for samples 54 and 56, and much larger for 61. These samples should then lie quite perceptibly below the theoretical curve for lattice and impurity scattering. Samples 54 and 56 are, however, well above the $m/4$ curve. The minimum of μ_H/μ at 78° occurs at about 0.2 ohm cm, near sample 64. It is expected then that this sample will lie above the theoretical curve about 5 percent. It is about 20 percent above the $m/4$ curve, however. This sample does tend to lie higher than the others but only by about 8 percent. On the basis of these considerations, it can be seen that an effective mass of about $m/8$ provides a satisfactory fit at 78°. The same type of reasoning applied to the 150° data leads to an effective mass at that temperature between $m/6$ and $m/8$.

On the basis of the relative insensitivity of the fit to the effective mass value and the scatter of the data, it is apparent that not too much significance is to be attached to the particular effective mass values obtained. In particular, if the μ_H/μ values used are somewhat too high, as indicated by the drift mobility results, the m_n values stated are all high. This, however, will not wipe out the trend to increasing effective mass with temperature.

Since there is no other reason to believe that effective mass as such is changing in this way, these results are more significantly interpreted as indicating that μ_I does not vary with temperature as predicted by (4) or (5) but somewhat less rapidly. According to these results, the exponent of T in the numerator should be closer to 1.0 than 1.5.

It would appear desirable to check this result by computing $\mu_I(T)$ directly from $\mu(T)$ for the individual samples. Such a procedure would at first sight seem to have the additional advantage of being independent of μ_H/μ. Actually, however, this is not the case because it is necessary to know n to compute μ from σ. In any case, this type of approach is not useful because ionized impurity scattering is generally considered smaller than lattice scattering in these samples throughout this temperature range. Small errors in μ, therefore, whether experimental or from inaccuracy in μ_H/μ, lead to large errors in μ_I.

4.3 Temperature Range Below 78°K

In the temperature range below 78° detailed consideration was given to the data for 20.4°K and for 11.5°K, the latter being about the lowest temperature attained for most samples. At these temperatures lattice scattering, ionized, and neutral impurity scattering are all important. The relevant quantities about which information is desired are acceptor density and effective masses to be used in ionized and neutral impurity scattering formulas. We shall consider first the information which can be obtained about the latter. At 11.5° for all but the two purest samples carrier concentration is down to less than one percent of its 300° value, and the density of neutral donors is quite accurately equal to the saturation value of $N_D - N_A$. This enables one to set fairly accurately a lower limit for the effective mass to be used in neutral impurity scattering. The values of μ computed from the Erginsoy formula for m_n less than $m/4$ are less than the experimental Hall mobilities for the samples with large N_N, e.g., 64, 54, 56, 61. If lattice and ionized impurity scattering are also taken into account for these samples, this lower limit is pushed up to about $m/3$. An upper limit for the effective mass to be used in μ_N cannot be set with the same certainty. For the samples with small N_N the neutral impurity scattering provides only a small cor-

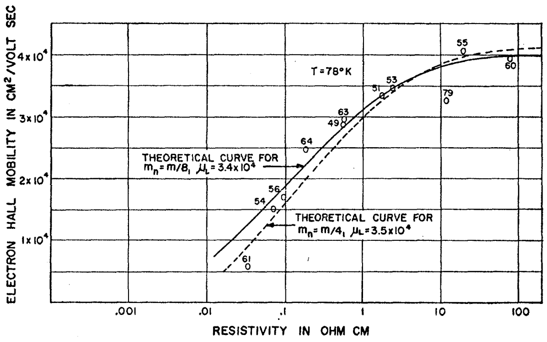

Fig. 9. Plots of experimental and theoretical Hall mobility *vs* resistivity at 78°K. Note, however, that the theoretical curves do not include neutral impurity scattering, which does affect samples 54, 56, and 61.

rection for m_n greater than $m/4$. In the samples with large N_N the observed mobilities can be fitted for any m_n greater than $m/4$ simply by adjusting the N_A values, which are of course unknown. For large enough m_n, however, these become unreasonably large. An upper limit to the effective mass can therefore be set by consideration of what is plausible in the way of acceptor concentration in these samples.

In the undoped, high-resistivity samples, such as 55, the temperature-dependence and the high mobility suggest that compensation of impurities is not taking place, and N_A should be somewhat less than the saturation value of N_D-N_A, or at most that order of magnitude. In the doped samples it is reasonable to expect N_A's of the same order of magnitude, or larger by perhaps a factor of 10 because the starting material before doping is not always purified to quite the same extent. On the basis of the stated chemical purity of the doping arsenic it is not expected that the doping process would add an amount of p-type impurity comparable to this residual concentration. Thus it appears reasonable to expect acceptor concentrations in the range $10^{12}/\text{cm}^3$ to $10^{14}/\text{cm}^3$ in all samples, with no particular correlation appearing between acceptor concentration and resistivity.

On this basis m_n should certainly be taken less than m in the Erginsoy formula. For $m_n=m$ there is a definite trend to increasing N_A with increasing N_N; the three most heavily doped nondegenerate samples requiring much larger values than the others to explain the observed mobilities. The values of m_n which lead to N_A values which best fit the criteria set up in the preceding paragraph are in the neighborhood of $m/3$.

In computing N_A the μ_N values were first obtained using an effective mass of $m/3$. These were used in (18) to calculate μ_{LI} from the observed mobilities. The impurity mobility was then computed from (16) with the lattice mobility taken as 8.0×10^5 cm²/volt sec, the value obtained by extrapolation of the high-temperature results (see Fig. 6). Because of the number of unknowns it is not possible to determine from the 11.5° data the value of effective mass to be used in μ_I. Although the high-temperature results are inadequate for extrapolation, it is a reasonable guess that if the high-temperaature trend were continued the effective mass at 11.5° would be $m/16$ or less. N_I values were calculated from μ_I using effective masses of $m/16$ and $m/4$. With n taken from the Hall data, N_I values were finally obtained from $(N_I-n)/2$. The deviation of μ_H/μ from 1 was neglected throughout in the calculation described.

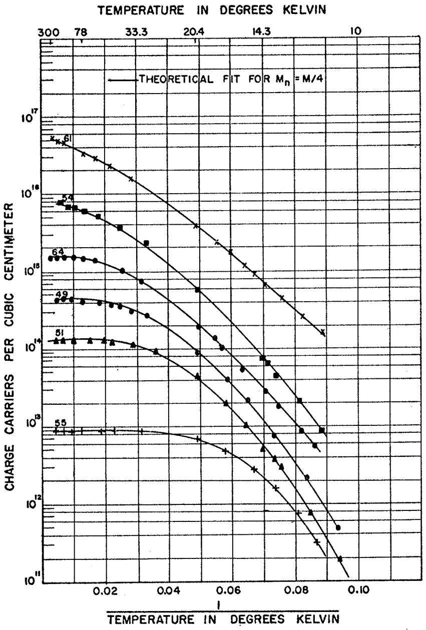

FIG. 10. Electron concentration as a function of inverse absolute temperature for a number of samples. The points are computed from the Hall data, and the solid lines are theoretical fits for an effective mass of $m/4$.

TABLE I. Calculated values of acceptor concentration.

Sample	Saturation N_D-N_A	N_A from mobility ($m/4$)	N_A from mobility ($m/16$)	N_A from concentration data
	1/cm³	1/cm³	1/cm³	1/cm³
55	1.0×10^{13}	4.8×10^{11}	1.3×10^{12}	$2\ \times10^{12}$
53	9.4×10^{13}	5.9×10^{11}	1.8×10^{12}	
51	1.4×10^{14}	9.6×10^{12}	2.2×10^{13}	7.3×10^{12}
63	4.6×10^{14}	2.5×10^{13}	5.8×10^{13}	$7\ \times10^{13}$
49	4.8×10^{14}	9.8×10^{12}	2.3×10^{13}	2.5×10^{13}
64	1.7×10^{15}	3.0×10^{11}	6.0×10^{12}	1.9×10^{13}
56	5.1×10^{15}	1.0×10^{14}	2.4×10^{14}	
54	7.5×10^{15}	3.6×10^{13}	1.0×10^{14}	1.5×10^{14}
61	5.5×10^{16}	1.3×10^{15}	4.7×10^{15}	2.0×10^{15}

This is sufficiently accurate for the purer samples because μ_H/μ values are quite close to 1 anyway. It would also be so for the less pure samples if their mobility were mainly determined by neutral impurity scattering. It was found, however, that ionized impurity scattering was quite important in some of the more heavily doped samples. In some cases, μ_H/μ values might be 1.5 or greater, and their inclusion would affect the N_A values considerably. A rough correction was made for this by computing another set of N_A values incorporating μ_H/μ values determined from μ_L/μ_I, and interpolating between the two sets according to the value of μ/μ_{LI} for the sample. This probably results in somewhat too large N_A for the more heavily doped samples. The N_A values so obtained are listed in Table I. Detailed consideration of the different samples shows that, despite uncertainties in the effective masses, the values listed for $m/16$ can be expected to be good within a factor 10 with the possible exception of samples 54 and 64. In the case of samples 51, 63, and 49 the N_A's are better determined, being probably correct within a factor 5. Semiquantitative verification of this set of N_A values is provided by comparison with the set obtained from carrier concentration data, which are also listed in Table I. These will be considered in the next section. This is unfortunately the only quantitative type of check available. Minority impurity concentrations of the size calculated should quite noticeably affect the mobility below 78°, but without knowledge of the effective masses this is not useful for a quantitative check. One small piece of verification is provided by the behavior of samples 63 and 49. These have almost identical values of saturation N_D-N_A and almost identical mobilities in the temperature range 78° to 300°, with 63 slightly higher than 49. The calculated N_A for 63, however, is more than twice that of 49 and this should make the 20.4° mobility of 63 about 10 percent lower than that of 49, which is the case experimentally. It can also be observed that the behavior of μ_H as a function of temperature is consistent with the calculated N_A's, samples 53 and 64 with relatively small N_A's showing the most pronounced s-shape, for example.

The indicated uncertainty in the N_A values coupled with the fact that their effect on μ_I might be as much as 40 percent at 20.4° rules out detailed calculations at that temperature. By the same type of consideration as previously employed it can be shown that the effective mass to be used in the ionized impurity scattering is less than $m/4$, while that for neutral impurity scattering lies between $m/6$ and m.

V. THEORY AND ANALYSIS OF CONCENTRATION DATA

5.1 Evaluation of Parameters Involved in Fit

The relation between electron concentration and temperature in the extrinsic region is given by[37]

$$\frac{n(N_A+n)}{N_D-N_A-n}=\left(\frac{2\pi m_n kT}{h^2}\right)^{\frac{3}{2}}\exp(-\mathcal{E}_D/kT),\tag{19}$$

where $\mathcal{E}_D$ is the amount of energy required to raise an electron from a donor level to the conduction band. For samples with impurity content of perhaps $10^{16}/\text{cm}^3$ or greater, $\mathcal{E}_D$ may be expected to vary somewhat with concentration and temperature. As is customary, however, the assumption that $\mathcal{E}_D$ is constant for a given sample was made in fitting all samples. The validity of this assumption will be examined later.

In attempting to fit the data, it was found that for a given sample the activation energy is determined within fairly narrow limits but the other two parameters are not. Since m_n is expected to be the same for all samples, outside the degenerate and near-degenerate ranges at any rate, the criterion of best fit for all samples was used to choose an m_n value. This gave a value of $m/4$. The fitted curves for this mass are shown in Fig. 10. Curves which do not fit too badly can be obtained for values of m_n in the range from $0.2m$ to $0.5m$, but masses in the neighborhood of $m/4$ give the best results.[38] The N_A values used in the curves shown are listed in Table I. They are all within a factor 3 of those determined for $m/16$ in the low-temperature mobility. Since the latter are only good within a factor 5 or 10, this constitutes reasonable agreement and additional support for a value in the neighborhood of $m/4$. The $\mathcal{E}_D$ values obtained from fitting these curves are plotted *vs* N_D-N_A in Fig. 11.[39] As previously mentioned, the $\mathcal{E}_D$ values are not very sensitive to the effective mass value chosen.

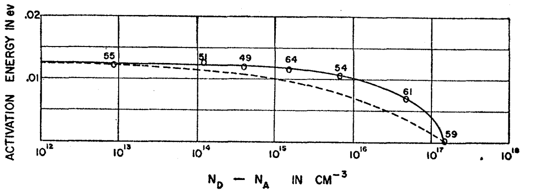

FIG. 11. Activation energy as a function of uncompensated donor concentration. The solid line represents the variation found experimentally, the dashed line the type of variation found experimentally for silicon: $\mathcal{E}_D(N_D)=\mathcal{E}_D(0)-\alpha N_D^{\frac{1}{3}}$.

As mentioned in a previous section, the experimental data in Fig. 10 represent $1/Re$ rather than carrier concentration. It can be shown that the effect on the activation energy of neglecting μ_H/μ is small for these samples. The activation energy is essentially determined by the slope of n *vs* $1/T$ over a small range of temperatures, roughly 15°K to 11°K. For the purer samples the change in μ_H/μ in this range can be calculated with reasonable accuracy from (15), and is less than 15 percent. Inclusion of μ_H/μ would thus lead to alteration of the slope and $\mathcal{E}_D$ of less than 15 percent for these samples. For more impure samples the error would be much larger if it were not for the presence of appreciable neutral impurity scattering. This will cut down the μ_H/μ values, and therefore the correction to the slope.

According to the hydrogen-like model of a donor, the binding energy of an electron is given by

$$\mathcal{E}_D=\frac{13.6}{\kappa^2}\frac{m_n}{m}=0.052\frac{m_n}{m}\tag{20}$$

for germanium. From the curve-fitting described, an $\mathcal{E}_D$ value of 0.0125 ev is obtained for the purer samples.

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[37] J. H. DeBoer and W. C. van Geel, Physica 2, 186 (1935). This form takes into account trapping of the electrons by the ground state of the donors only, $\mathcal{E}_D$ being the distance of the ground state below the edge of the conduction band. On the hydrogen-like model, the excited states all lie within $\mathcal{E}_D/4$ of the conduction band. At temperatures such that $kT\ll\mathcal{E}_D$, trapping by these excited states will be negligible compared to trapping by the ground state and (19) is valid. In what follows only this temperature range is used in determining the parameters in (19).

[38] Note, however, that sample 56 showed anomalous behavior in that it could not be fitted well with any set of parameters, but better-fitting curves were obtained with effective masses of the order of m than with $m/4$. This sample was cut from near the tip end of a single crystal, had a relatively large N_A, and may have been quite nonuniform in impurity distribution.

[39] Sample 59, the lowest concentration sample for which $\mathcal{E}_D$ was zero, was unfortunately not prepared as were the others discussed and may not have been arsenic-doped. The lowest concentration sample in the series which had vanishing $\mathcal{E}_D$ had a concentration of about $3\times10^{17}/\text{cm}^3$. This sample is not included because, unfortunately, complete data are not available.

Substituted in (20) this gives an m_n of $m/4$, which is just in the range of m_n values found to give the best agreement with the concentration data. It can thus be said that at least approximate equality of these effective masses has been established. This is significant in that equality is what would be expected on the usual simple picture of the band structure and energy surfaces but was not necessarily expected for the more complicated case.

5.2 Variation of Activation Energy with Concentration

Before comparing the observed variation of activation energy with theoretical predictions, it is worth noting that these results do not agree with those found by Pearson and Bardeen for p-type silicon.[40] In that case it was found that the variation of activation energy with concentration followed closely an equation of the type

$$\mathcal{E}_D(N_D)=\mathcal{E}_D(0)-\alpha N_D^{\frac{1}{3}}, \tag{21}$$

where $\alpha=4.3\times 10^{-8}$. In checking whether these data follow such an equation, it is necessary to take $\alpha=2.35\times 10^{-8}$ to make $\mathcal{E}_D$ vanish at $1.5\times 10^{17}/\text{cm}^3$. The resulting $\mathcal{E}_D(N_D)$ is plotted in Fig. 11. (Actually it is plotted *vs* N_D-N_A rather than N_D, but this makes little difference.) It is apparent that it does not agree well with these experimental results. It can furthermore be shown that this conclusion is not dependent on the value of effective mass chosen for fitting within the range of reasonably good fitting, of course.

There are three types of effect which have been considered to explain the variation of activation energy with concentration. We shall first consider the mechanism investigated by Pearson and Bardeen and subsequently by Castellan and Seitz,[41] in attempting to explain the empirical result (21). They suggested that the decrease of activation energy with concentration was due to the potential energy of attraction between the ionized donors and conduction electrons. This mechanism, they considered, would lead to a lowering of activation energy inversely proportional to the average distance between an electron and an ion, thus essentially proportional to the $\frac{1}{3}$-power of the density of ionized donors. It is apparent that this leads to a variation of activation energy with degree of ionization, in which case the assumption of constant $\mathcal{E}_D$ is of course not valid. Since the $\mathcal{E}_D$ values are determined by the fit to the low-concentration part of the experimental curve, they must represent values characteristic of the low-concentration region. The previous theory would then predict that the $\mathcal{E}_D$ values vary according to an equation of the form (21) with N_D replaced by the average density of ionized donors in the low-concentration or low-temperature region.[42]

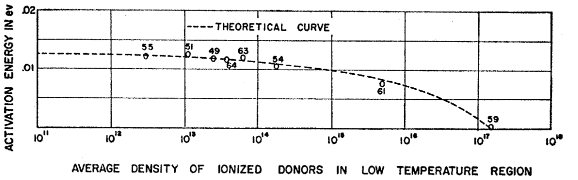

FIG. 12. Activation energy as a function of the average density of ionized donors in the temperature interval used for fitting. The dashed line represents the theoretical variation predicted by Eq. (21) with N_D replaced by the average density of ionized donors in the fitting interval, and repulsion of acceptors neglected.

In comparing this prediction with experimental results it is necessary to take account of the fact, so far neglected, that there are present both ionized donors and ionized acceptors, with densities N_A+n and N_A, respectively. At the low temperatures in question N_A is, in fact, usually larger than n and ionized donor and ionized acceptor concentrations may be approximately equal. It is reasonable to expect that N_A negatively charged acceptors will not cancel the effect of N_A positively charged donors. In the presence of both, an electron would tend to concentrate around the positive charges and avoid the negative charges, particularly at low temperatures, and thus obtain a lowering of its average potential energy.

Some information about the relative importance of this mechanism can be obtained by neglecting the repulsion of the acceptors and plotting $\mathcal{E}_D$ *vs* average density of ionized donors in the region from which the $\mathcal{E}_D$ value was obtained. Such a plot is shown in Fig. 12. N_A values were taken as the mean of those obtained from mobility and concentration data. The average value of n over the region involved in fitting, obviously a poorly defined quantity, is fortunately small compared to N_A in almost all cases. Also shown is a plot of $\mathcal{E}_D$ from the theoretical equation (21) with N_D replaced by the average density of ionized donors. The value of α required for fit at the high-concentration end is about that obtained in a crude estimate of the effect by Pearson and Bardeen and by Castellan and Seitz. Although this curve certainly overestimates the lowering predicted by the previous theory, the significant experimental points lie a little lower than the curve. It would appear that this mechanism can account for part of, but not all, the observed decrease in activation energy.

It was pointed out by Pincherle,[43] and by James and Lehman, that free carriers will also give rise to a decrease in activation energy by screening the field around a trapping center. The effectiveness of screening and therefore the amount of the decrease will be greater at lower temperatures and higher electron concentra-

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[40] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

[41] G. W. Castellan and F. Seitz, "On the energy states of impurities in silicon," published in *Semi-Conducting Materials* (Butterworths Scientific Publications, London, 1951).

[42] For this reason, it was pointed out by Castellan and Seitz, this mechanism does not explain the Pearson and Bardeen experimental result (21).

[43] L. Pincherle, Proc. Phys. Soc. (London) **A64**, 663 (1951).

tions. Calculations indicate that the effect is considerable in silicon; it can be expected to be significant for germanium also.

Another source of lowering of the activation energy lies in polarization effects. A germanium specimen with neutral donors, for example, has a higher dielectric constant than a pure one. A free electron in the impure specimen can give rise to a greater polarization, lowering the edge of the conduction band and consequently the activation energy. A crude evaluation of the size of these effects was carried out for the case of silicon by Castellan and Seitz.[41] They assumed that the polarizability of a neutral donor was that of a hydrogen atom with effective nuclear charge equal to the reciprocal of the dielectric constant of silicon. The hydrogen-like model can be modified quite analogously to allow for an effective mass different from the free-electron mass. An m_n/m ratio less than 1 increases the polarizability, and thus the size of the effect. The analysis of Castellan and Seitz applied to germanium, with an effective mass of $m/4$, leads to a lowering of $\mathcal{E}_D$ for sample 61, which has an N_D-N_A of $5\times10^{16}/\text{cm}^3$, of about 0.001 ev. For samples with higher impurity concentration the effect would be greater. This indicates that polarization effects, although probably smaller than the others, must also be taken into account in explaining the experimental results.

It is of interest to consider the variation of activation energy with temperature to which the three effects cited give rise. In the case of the screening effect the temperature dependence arises from the dependence on carrier concentration and from the fact that the fraction of the time spent by electrons around the positive charges depends on their kinetic energy. The variation in activation energy due to this effect might be considerable over the temperature interval important in determining $\mathcal{E}_D$. In the limit of low temperature and vanishing concentration the decrease in $\mathcal{E}_D$ arising from this mechanism will vanish. The attraction of electrons to ionized donors will depend on temperature for the same reasons that the screening effect does, but will also depend greatly on the minority impurity concentration in the individual sample. The variation of $\mathcal{E}_D$ with temperature due to this mechanism should be relatively small at temperatures such that the conduction electron concentration is less than N_A. This is the case, for example, over the temperature interval from which the $\mathcal{E}_D$ value is determined and at all lower temperatures in the case of sample 61. This mechanism gives a decrease in activation energy which does not vanish in the limit of low-temperature and low-electron concentration. Polarization effects differ from the other two in that they will be largest in this limit and will vary significantly with temperature only at temperatures higher than those involved in obtaining the $\mathcal{E}_D$ values. It can be seen that the way in which $\mathcal{E}_D$ varies with temperature will depend on the relative importance of the three effects, which in turn may be different in different temperature ranges. Study of the Hall constant at lower temperatures may be useful in separating the effects.

It is usually considered that metallic conduction, or the vanishing of activation energy, will set in around concentrations such that half the average distance between donor impurities is equal to the radius of the bound electron orbit.[41] This statement can be somewhat refined by assuming the impurities uniformly spaced so they can be surrounded by imaginary spheres all of the same radius r_s chosen so that the spheres fill all space. In terms of this, the criterion for vanishing $\mathcal{E}_D$ could be stated thus: r_s must equal the average distance of the bound electron from the center of the sphere. This condition is not at all satisfied in the case of p-type silicon,[40] where for the lowest concentration at which metallic conduction is observed r_s is approximately five times this distance. For n-type germanium and an effective mass of $m/4$, r_s for the lowest concentration at which metallic conduction is observed is approximately twice this distance. To satisfy the criterion stated previously a concentration of $2\times10^{18}/\text{cm}^3$ would be required. It is to be expected that randomness of the impurity distribution will cause the onset of metallic conduction at lower concentrations than required by the above criterion; it is possible that this effect can account for this discrepancy.

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