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Electrical Properties of Pure Silicon and Silicon Alloys Containing Boron and Phosphorus

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Electrical resistivity and Hall measurements have been made over the temperature range from 87° to 900°K on pure silicon and on silicon alloys containing from 0.0005 to 1.0 percent boron (p-type impurity) or phosphorus (n-type impurity). X-ray measurements indicate that both elements replace silicon in the lattice. It is shown that each added boron atom contributes one acceptor level, and it is likely that each added phosphorous contributes a donor level.

The temperature variation of the concentrations of carriers, electrons and holes, and of their mobilities, are determined from the resistivity and Hall data for the different samples. In the intrinsic range, at high temperatures, conductivity results from electrons thermally excited from the filled band to the conduction band. The energy gap is about 1.12 ev. The product of electron and hole concentration at any temperature is

$$n_e n_h = 7.8\times 10^{32} T^3 \exp(-12{,}900/T).$$

In the saturation range, which occurs just below the intrinsic range, the concentrations are independent of temperature. All donors (or acceptors) are ionized and the concentration of carriers is equal to the net concentration of significant impurities (P or B).

The energy, E_A, required to ionize an acceptor by exciting an electron from the filled band, as determined from the temperature variation of concentration at lower temperatures, decreases with increasing impurity concentration and vanishes for concentrations above $5\times 10^{18}/\text{cm}^3$. The value of E_A at high dilution, 0.08 ev, is about what is expected for a hole moving in a hydrogen-like orbit about a substitutional B^- ion. The decrease in E_A with increase in concentration is attributed to a residual potential energy of attraction between the holes and impurity ions. The ionization energy of donors is less than that of acceptors, probably because conduction electrons have a smaller effective mass than holes. In samples with large impurity concentrations the carriers form a degenerate gas at low temperatures, and the resistivity and Hall coefficient become independent of temperature.

At high temperatures the mobilities of electrons and holes approach the values

$$\mu_e = 3.0\mu_h = 15\times 10^5 T^{-\frac{3}{2}} \text{ (cm}^2\text{/volt sec.)}.$$

These values are determined by lattice scattering and are independent of impurity concentration. At lower temperatures scattering by both ionized and neutral impurity centers contribute, and the mobility is largest for the more pure samples. Impurity scattering increases rapidly with decrease in temperature and the mobility passes through a maximum which depends on impurity concentration. Theories of impurity scattering of Conwell and Weisskopf, of Johnson and Lark-Horovitz, and of Mott give mobilities which agree as to order of magnitude with the observed.

I. INTRODUCTION

ELECTRICAL resistivity and Hall measurements have been made over a temperature range from 87°K to 900°K on a number of silicon samples to which known amounts of boron and phosphorus have been added.[1] Both enter substitutionally, boron acting as an acceptor impurity and phosphorus as a donor. The data are analyzed to determine the variation of concentration of current carriers and mobility with impurities and temperature. The results are interpreted in terms of existing theories of conduction in semiconductors. The analysis is similar to that applied by Lark-Horovitz and Johnson to the conductivity in germanium.[2] Our results are more complete, particularly as regards the wide range of impurity concentrations, than previous measurements on silicon made at the Universities of Pennsylvania[3] and Purdue.[4]

1.1 Energy Levels in Silicon

Silicon is an element of the fourth group of the periodic table, with the same crystal structure as diamond. Each silicon atom has four near neighbors with which it forms covalent bonds in a tetrahedral configuration. The specific gravity is about 2.4 and the melting point 1420°C. The

[1] A preliminary account of this work was presented by the authors at the Am. Phys. Soc. meeting in New York, January, 1948. See Phys. Rev. **73**, 1256A (1948). Earlier measurements are described by G. L. Pearson and W. Shockley, Phys. Rev. **71**, 142A (1947).

[2] K. Lark-Horovitz and V. A. Johnson, Phys. Rev. **69**, 258A (1946).

[3] F. Seitz, *The Electrical Conductivity of Silicon and Germanium* (NDRC 14–110, University of Pennsylvania, November 3, 1942).

[4] Unpublished measurements of W. W. Scanlon and others.

dielectric constant is about 13. The conductivity at room temperature depends on the presence of impurities. It is estimated that ideally pure silicon would have a resistivity of about 10^6 ohm cm.

Considerable progress was made in understanding the nature of the significant impurities by research done during the war in connection with the development of rectifiers for radar uses.[5] Scaff, Theuerer, and Schumacher[6] of the metallurgical group of the Bell Laboratories have found that elements of the third group, such as boron and aluminum, give defect or *p*-type conductivity. Elements from the fifth group, such as phosphorus, antimony, and arsenic, give excess or *n*-type conductivity. Impurities which give *p*-type conductivity are called acceptors; those which give *n*-type conductivity, donors. We shall give x-ray evidence that boron and phosphorus enter substitutionally into the lattice. Probably the other significant impurities also occupy substitutional rather than interstitial positions.

A substitutional impurity atom from the fifth group has one more valence electron than is required to fill the four valence bonds with neighboring silicon atoms. In its lowest energy state, this extra electron is weakly bound by the extra charge on the nucleus of the impurity atom. The electron moves in a hydrogen-like orbit,[7] but the electrostatic attractive force is reduced by the dielectric constant, κ, of the crystal. The effect is to reduce the binding energy by a factor κ^2, which brings it down to the range of thermal energies ($\sim$0.08 ev). This means that a large fraction of the impurity atoms are thermally ionized at room temperature, and the electrons thus freed contribute to the conductivity.

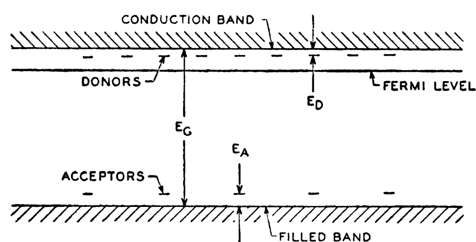


FIG. 1. Schematic energy level diagram for silicon.

A trivalent impurity atom, such as boron, has one less electron than is required to fill the valence bonds.[8] The position from which the electron is missing may shift from one valence bond to another in the crystal by motion of an electron in the opposite direction. The missing electron, or hole, behaves in all respects like a particle with a positive charge equal in magnitude to the electron charge. It has inertia, momentum, and energy corresponding to a mass of the same order as the mass of an electron. Thus one speaks of the velocity, mobility, and kinetic energy of a hole moving through the crystal in just the way one speaks of the corresponding quantities for excess or conduction electrons. The only essential difference is in the sign of the mobile charge.

The extra electron required to fill the valence bonds about the trivalent impurity gives the atom an effective negative charge, so that it becomes in effect a negative ion. In its lowest state, the positive hole will be weakly bound by the electrostatic field of the negative ion and will move in a hydrogen-like orbit similar to that of the excess electron discussed above. The ionization energy, that is, the energy required to free the hole from the negative ion so that it is free to contribute to the conductivity, is likewise of the order of thermal energy. At room temperature the majority of the acceptor impurities will be dissociated into holes and negative ions.

If sufficient energy is available, an electron can be removed from a normal valence bond to a distant place in the crystal. Both the electron so freed and the place of the missing electron, or hole, left behind are free to take part in conduction. The energy required is about 1.12 ev in silicon.[9] Electrons and holes may be so produced by light quanta of sufficient energy, or by thermal excitation at high temperatures. In the intrinsic

[5] J. H. Scaff and R. S. Ohl, Bell Sys. Tech. J. **26**, 1 (1947). A comprehensive review of the work done during the war under the NDRC is given by H. C. Torry and C. A. Whitmer, *Crystal Rectifier* (McGraw-Hill Book Company, Inc., New York, 1948). This book will be referred to as T-W.

[6] J. H. Scaff, H. C. Theuerer, and E. E. Schumacher, "*P*-type and *N*-type silicon and the formation of the photovoltaic barrier in silicon" (to be published in Trans. A.I.M.E.).

[7] See N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 166. For application to silicon, see T-W, p. 66.

[8] See T-W, p. 65.

[9] This value, derived from the present experiments, agrees with earlier values of Seitz (reference 3) and of G. K. Teal, J. R. Fisher, and A. W. Treptow, J. App. Phys. **17**, 879 (1946).

conductivity range there are equal concentrations of electrons and holes determined by a balance between those formed by thermal excitation and those recombining. The recombination, of course, corresponds to excess or conduction electrons dropping back into vacant valence bond positions. The intrinsic conductivity range occurs at temperatures so high that the numbers of electrons or holes arising from impurities is small compared with the total number present.

The energy relations are illustrated in the energy level diagram[10] shown schematically in Fig. 1. The diagram shows the allowed energy levels for the valence electrons in a silicon crystal. There is a continuous band of levels, the filled band, normally occupied by the electrons in valence bonds, an energy gap of 1.12 ev in which there are no levels of the ideal crystal, and then another continuous band of levels, the conduction band, normally unoccupied. There are just sufficient levels in the filled band to accommodate the four valence electrons per atom. The acceptor impurity levels lie just above the filled band and the donor levels just below the conduction band. The donors are normally neutral, but become positively charged when ionized by excitation of an electron to the conduction band. The acceptors are normally neutral, but become negatively charged when occupied by electrons excited from the filled band.

1.2 Preparation of Samples

The silicon used in these studies was obtained from E. I. du Pont de Nemours Company. It is in the form of long needles and was prepared from silicon tetrachloride by pyrolytic reduction with zinc.[11] The purity is very high—about 99.97 percent with some variation between lots as shown by spectroscopic analysis. The subsequent forming with the addition of known amounts of boron or phosphorus was done by J. H. Scaff and H. C. Theuerer of the metallurgical group of the Bell Telephone Laboratories. The steps which have been described in detail[6] include (1) careful determination of the weights of the raw materials, (2) melting the charge in a silica crucible by means of an induction furnace in an atmosphere of helium, and (3) solidifying into an ingot by a precisely controlled temperature cycle.

TABLE I. Composition of silicon alloys.

I	II	III	IV	V	VI	VII
Sample	Solute	Weight percent of solute	Atomic percent of solute	Atoms of solute per cc of melt	Carriers/cc of melt in saturation range	Carriers/atoms of solute
1	——	0.0	0.0	0.0	8.0×10^{15}	α
2	Boron	0.0005	0.0013	6.7×10^{17}	6.0×10^{17}	0.90
3	Boron	0.001	0.0026	1.3×10^{18}	1.3×10^{18}	1.00
4	Boron	0.002	0.0052	2.7×10^{18}	2.5×10^{18}	0.93
5	Boron	0.005	0.013	6.7×10^{18}	5.3×10^{18}	0.79
6	Boron	0.01	0.026	1.3×10^{19}	1.4×10^{19}	1.08
7	Boron	0.1	0.26	1.3×10^{20}	1.2×10^{20}	0.93
8	Boron	1.0	2.6	1.3×10^{21}	4.8×10^{20}	0.37
A	Phosphorus	0.001	0.00091	4.7×10^{17}	1.05×10^{17}	0.22
B	Phosphorus	0.0057	0.0072	2.7×10^{18}	1.25×10^{18}	0.46
C	Phosphorus	0.1	0.091	4.7×10^{19}	1.7×10^{19}	0.36
D	Phosphorus	1.0	0.91	4.7×10^{20}	2.6×10^{20}	0.55

The ingot was cut into thin slabs approximately 2 cm×0.5 cm×0.1 cm with a diamond wheel and the surfaces smoothed by lapping with 600 mesh carborundum and water. Metallic electrodes were applied by means of the electrolytic deposition of rhodium. The entire surface was usually plated and, after protecting the desired sections, the excess was removed with an air blast containing 180-mesh carborundum grains. By this process non-rectifying electrodes as small as 0.02 cm in diameter were prepared which remained intact over the entire temperature range from 87 to 900°K in an atmosphere of air.

Using the methods described above, samples having the compositions listed in columns 1–5 of Table I were prepared.

1.3 Lattice Spacings of Silicon Alloys Containing Boron and Phosphorus

In order to determine whether boron and phosphorus enter the silicon lattice in a sub-

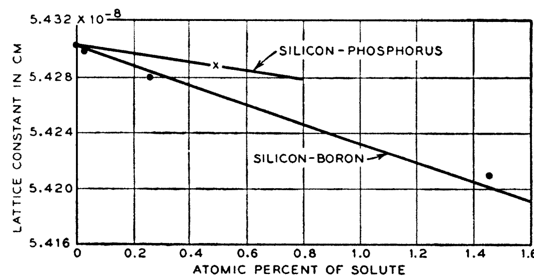


FIG. 2. Lattice constants of silicon-phosphorus and silicon-boron alloys at 25°C as determined from x-ray data.

[10] Cf. T-W, p. 49. A quantum-mechanical calculation of the energy bands in silicon is given by J. F. Mullaney, Phys. Rev. **66**, 326 (1944).

[11] The method used by du Pont for purifying silicon is described in T-W, p. 301.

stitutional or an interstitial manner, a study was made of the lattice spacing of these alloys as a function of the impurity content. Since the atomic radii of silicon, boron, and phosphorus are 1.17, 0.89, and 1.10×10^{-8} cm, respectively, it is predicted by Vegard's law that if the process is by substitution the addition of boron should shrink the lattice appreciably, while phosphorus should produce only a slight shrinkage. If these atoms enter the interstices between the silicon atoms, however, both should expand the lattice with phosphorus having a greater effect.

The lattice spacing measurements, performed by E. S. Greiner of the metallurgical group of the Bell Telephone Laboratories, were obtained by back reflection x-ray diffraction from powdered samples containing varying amounts of boron or phosphorus. The results, given in Fig. 2, show that both impurities contract the silicon lattice and that boron has the greater effect. Microscopic examination of alloys containing more than 0.5 percent boron by weight showed that a second phase appears and deposits on crystal grain boundaries.

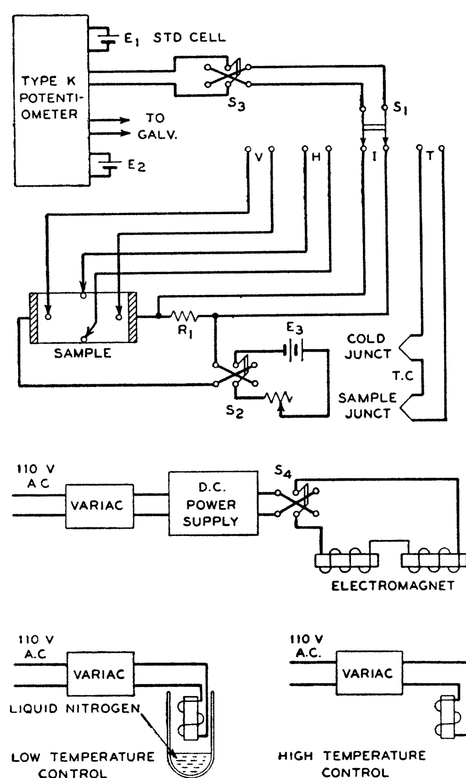


FIG. 3. Circuit diagram of equipment for measuring resistivities and Hall coefficients at different temperatures.

The results of this study indicate, therefore, that for small concentrations a substitutional solid solution of either boron or phosphorus is formed in silicon. That each added boron atom contributes an acceptor level is shown by a comparison of columns V and VI of Table I. There is evidence that not all the phosphorus added goes into solution, which accounts for smaller numbers of carriers for these samples.

II. EXPERIMENTAL PROCEDURE

The fundamental experimental data obtained in this study are the resistivity and Hall voltage as a function of temperature for each of the several alloy samples. Resistivity was measured by the potential probe method, Hall effect from the transverse voltage in a magnetic field, and temperature by the thermoelectric voltage of a Chromel-Alumel thermocouple.

A Leeds and Northrup Type K potentiometer in conjunction with a selector switch was used to measure all of these d.c. voltages. A rotating coil driven by a synchronous motor was used for measuring the magnetic field strengths. The indicating instrument for the a.c. measurement was a Weston model 622 voltmeter, and the system was calibrated with a permanent magnet whose field strength had been measured at the National Bureau of Standards. The desired temperatures were obtained by heating coils operating either in a thermos bottle containing liquid nitrogen for the low values, or in an electrically heated ceramic tube for the high values. Temperature gradients were avoided by placing the samples in good thermal contact with a non-magnetic metal block.

Figure 3 is a circuit diagram of the entire measuring circuit. The electrode arrangement of the sample is as shown, with contact being made to the rhodium by platinum-rhodium springs which held their tensile strength over the entire temperature range. The current through the sample is determined from the voltage drop across the fixed resistor R_1. The sample current, as well as the magnetic field polarity, may be reversed by switches S_2 and S_4. Measurements for both directions of these quantities are required to eliminate spurious thermal effects.

After showing the Hall effect to be a linear function of magnetic field strength over a wide range, a field strength of 4000 gauss was chosen for most of the measurements. The current through the sample was regulated to give the most advantageous voltage readings and was usually between 0.1 and 10 milliamperes. At low temperatures this current was reduced to avoid Joule heating and at high temperatures, especially in the high impurity samples, it was increased in order to raise the Hall voltage to a detectable level. It was the reduction of the Hall voltage at high temperatures which limited our Hall measurements to temperatures below 800°K for the high purity silicon and to still lower temperatures for the samples to which large amounts of boron or phosphorus had been added.

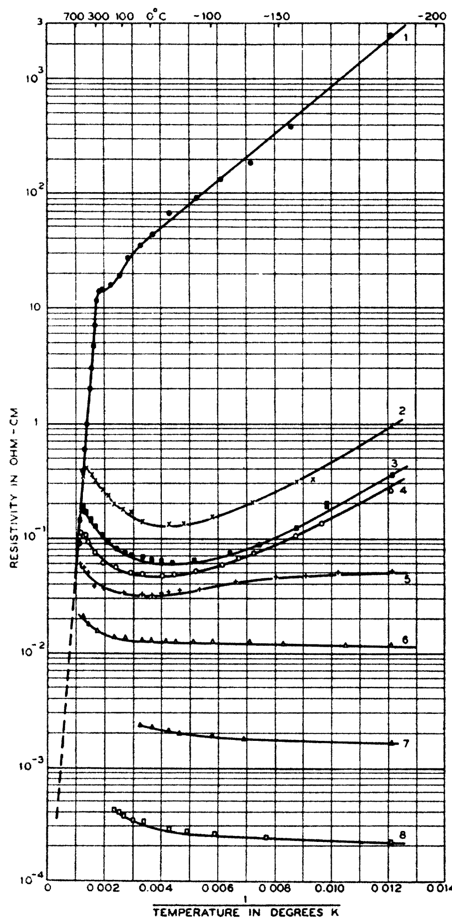


FIG. 4A. Resistivity of silicon-boron alloys as a function of the inverse absolute temperature. Compositions are given in Table I.

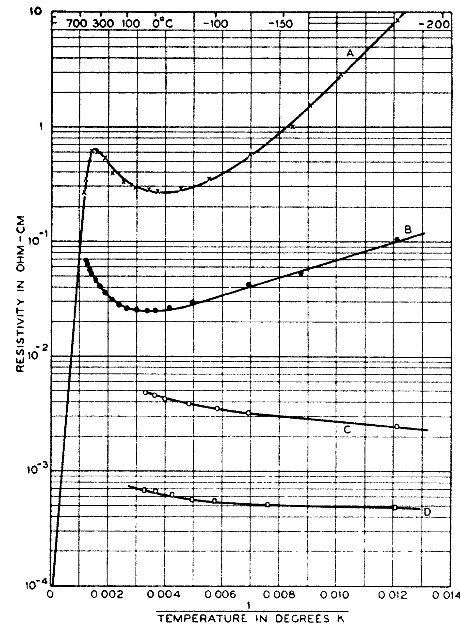


FIG. 4B. Resistivity of silicon-phosphorus alloys as a function of the inverse absolute temperature. Compositions are given in Table I.

III. EXPERIMENTAL RESULTS

The resistivities of the silicon-boron alloys are shown as a function of temperature in Fig. 4A. Curve 1 is for the high purity du Pont silicon to which no impurity was deliberately added and curves 2–8 are for silicon to which the specified amounts of boron (expressed in weight percents) had been introduced in the melt. The temperature range is from 700°C to -190°C, and the resistivity limits are from 2×10^3 ohm cm for the high purity silicon to 2×10^{-4} ohm cm for the one percent boron alloy.

At high temperatures the resistivities all fall on the same straight line. This is the intrinsic region in which there are approximately equal concentrations of electrons and holes. At lower temperatures the resistivity depends on the impurity content, increasing amounts of boron giving lower resistivity. Since sample No. 1 does not follow the intrinsic line at the lower temperatures, it is concluded that residual impurity atoms of unknown elements are present in the melt. The rapid decrease of resistivity with temperature in the intrinsic range results from the increase in concentration of electrons and holes which arise from thermal excitation of electrons

from the filled to the conduction band. Theory indicates (see Section 5.3) that the resistivity ρ expressed in ohm cm should vary as

$$\rho = A\epsilon^{E_G/2kT}, \quad (1)$$

where A is a constant, k is Boltzman's constant (8.69×10^{-5} ev/deg.), T is the temperature in degrees Kelvin, and E_G is the separation in electron volts between the top of the filled band and the bottom of the conduction band. From a fitting of the experimental data, we conclude that the value of E_G for silicon is 1.12 electron volts and the value of the constant A is 1.1×10^{-4} ohm cm.

The resistivity of the silicon-phosphorus alloys is shown as a function of temperature in Fig. 4B. These curves have the same general shape as those for the silicon-boron series and the intrinsic line is identical.

Hall voltages of the various samples were measured as a function of temperature and the Hall coefficient R, in cm³/coulomb, calculated from the relation

$$R = 10^{-8}\, V_H t/HI, \quad (2)$$

where V_H is the measured Hall voltage in volts, t the thickness of the sample in cm, H the magnetic field in gauss, and I the current in amperes.[12] As stated above, the measurements were taken with the field first in one direction and then in the other to eliminate false thermoelectric effects. The sign of the Hall coefficient was determined from the polarities of I, H, and V_H.

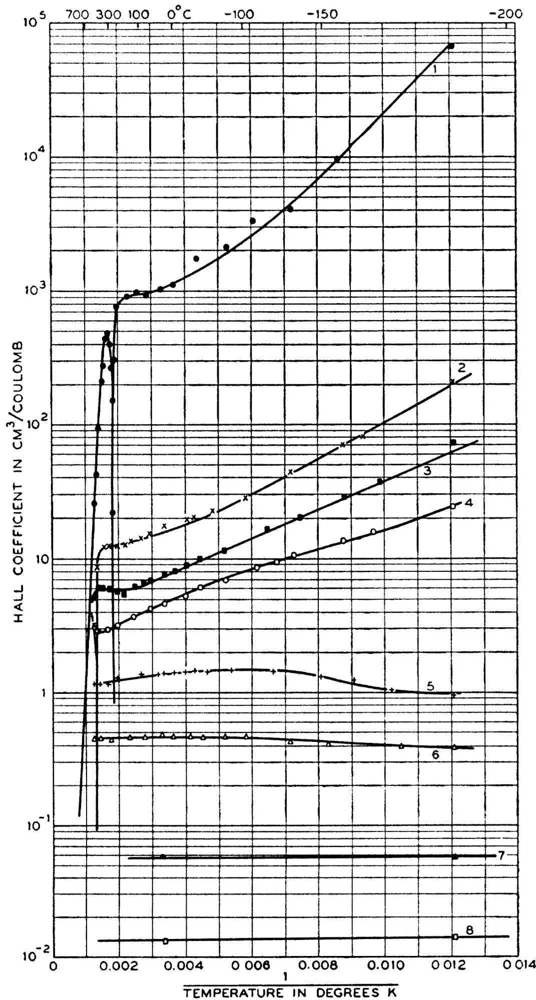


FIG. 5A. Hall coefficient in silicon-boron alloys as a function of the inverse absolute temperature. Compositions are given in Table I.

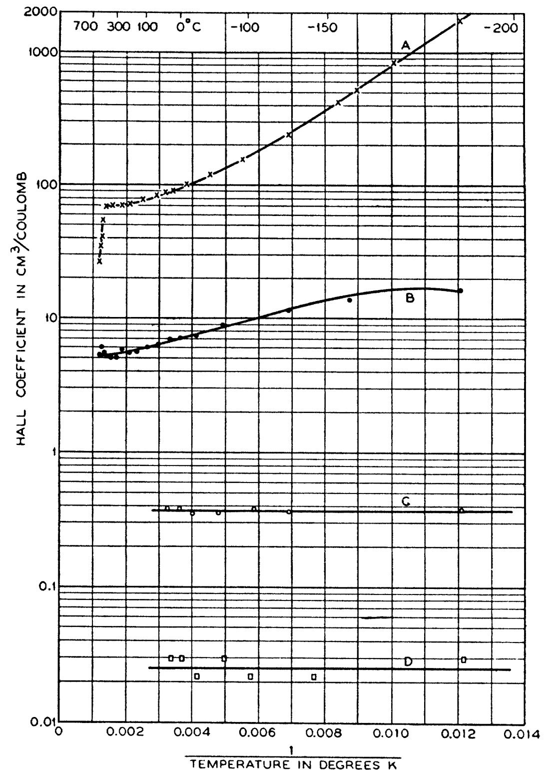


FIG. 5B. Hall coefficient in silicon-phosphorus alloys as a function of the inverse absolute temperature. Compositions are given in Table I.

[12] The length to width ratio of our samples was around 4. This is sufficient to eliminate the errors due to short circuiting of the current electrodes as described by I. Isenberg, B. R. Russell, and R. F. Greene, Phys. Rev. **74**, 1255(A) (1948).

Figure 5A is a plot of Hall coefficient as a function of temperature for the boron-silicon alloys. In each case the sign of the coefficient was positive in the low temperature or impurity conduction region, which indicates that boron is an acceptor impurity in silicon. For the purer samples No. 1 and No. 2 the coefficient reduced to zero and went negative in the intrinsic range. This negative sign in the region where electrons and holes are present in comparable numbers arises from the fact, as will be discussed in more detail in a following section, that electrons have a greater mobility than the holes.

Figure 5B is a plot of Hall coefficient as a function of temperature for the silicon-phosphorus alloys. The sign of the coefficient is negative at all temperatures, indicating that phosphorus is a donor impurity in silicon.

IV. CONCENTRATIONS AND MOBILITIES

Having measured the resistivity and Hall coefficient as a function of temperature for the two silicon alloy systems, it is now possible to calculate the following additional quantities as a function of temperature for either holes or electrons: (1) the number n per cm³, (2) the mobility μ in cm²/volt-sec., and (3) the mean free path l in cm. In Section 4.1 we deal only with non-degenerate cases, i.e., low densities of holes or electrons at medium and high temperatures. The degenerate cases are considered in Section 4.2.

The following notation is used:

e = magnitude of electronic charge = 1.6×10^{-19} coulomb.
n_e = concentration of conduction electrons (no./cm³).
n_h = concentration of holes (no./cm³).
N_D = concentration of donor impurities (no./cm³).
N_A = concentration of acceptor impurities (no./cm³).
μ_e = mobility of conduction electrons (cm²/volt sec.).
μ_h = mobility of holes (cm²/volt sec.).
$c=\mu_e/\mu_h$ = ratio of mobilities.
σ = conductivity (ohm⁻¹ cm⁻¹).
$\rho=1/\sigma$ = resistivity (ohms cm).
R = Hall coefficient (cm³/coulomb).
l_e = mean free path of electrons (cm).
l_h = mean free path of holes (cm).
E_G = energy gap between filled and conduction bands.
E_D = energy difference between donor level and conduction band.
E_A = energy difference between acceptor level and conduction band.
m = mass of electron in free space = 9.03×10^{-28} grams.

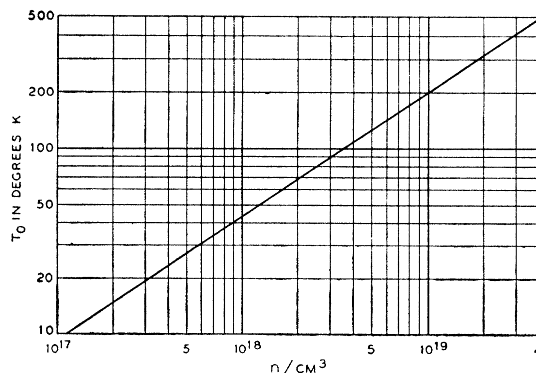


FIG. 6. Degeneracy temperature in degrees absolute as a function of electron density.

m_e = effective mass of conduction electrons (grams).
m_h = effective mass of holes (grams).
k = Boltzman's constant = 1.37×10^{-16} erg/degree.
T = absolute temperature (°K).
h = Planck's constant = 6.55×10^{-27} erg-sec.
$n_s=|N_A-N_D|$ = saturation concentration of holes or electrons (no./cm³).
κ = dielectric constant.
$E_0=(h^2/8m)(3n/\pi)^{\frac{2}{3}}$ = kinetic energy of electron (or hole) at the surface of the Fermi distribution.

4.1. Non-Degenerate Electron Gas

The basic equations required for the calculation of the mobility and concentration from measurements of the conductivity and Hall coefficient follow:[13]

(a) Impurity range:

$$\sigma=ne\mu, \tag{3}$$

$$R=\pm3\pi/8en=\pm7.4\times10^{18}/n, \tag{4}$$

$$n=\pm7.4\times10^{18}/R, \tag{5}$$

$$\mu=\pm(8/3\pi)\sigma R=\pm0.85\sigma R. \tag{6}$$

The positive signs apply to p-type and the negative to n-type conductivity.

(b) Intrinsic range:

$$\sigma=n_e e\mu_e+n_h e\mu_h, \tag{7}$$

$$R=-(3\pi/8e)([n_e c^2-n_h]/[n_e c+n_h]^2). \tag{8}$$

If $n_e=n_h=n$,

$$\sigma=ne(\mu_e+\mu_h), \tag{9}$$

$$R=-(3\pi/8ne)([c-1]/[c+1]), \tag{10}$$

$$n=-7.4\times10^{18}([c-1]/[c+1])/R. \tag{11}$$

[13] For methods of deriving the equations, see, for example, F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chapter IV. Cf. T-W, pp. 53–55.

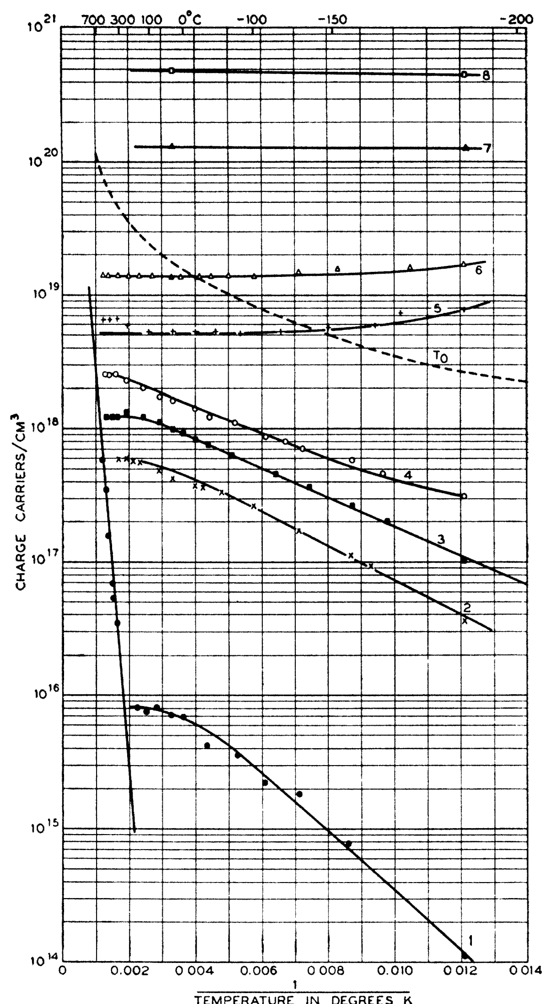


FIG. 7A. Number of charge carriers per unit volume in silicon-boron alloys as a function of the inverse absolute temperature. Compositions are given in Table I. T_0 is the degeneracy temperature.

The numerical factor $3\pi/8$ which occurs in the expressions for R, μ, and n is based on the assumption that the mean free path is independent of velocity. While this is true for scattering by lattice vibrations (thermal scattering), it is not true for scattering by impurities, which predominates at low temperatures. A different numerical factor should be used in the impurity scattering range[14] and intermediate values used when both lattice and impurity scattering are important. For simplicity, we neglect these variations and use the factor $3\pi/8$ throughout.

[14] If the mean free path varies with electron velocity as v^p, the factor is $3\pi^{\frac{1}{2}}\Gamma(p+3/2)/4(\Gamma(p/2+2))^2$, which reduces to $3\pi/8$ for $p=0$. For scattering by impurity ions, $p\sim 4$ and the factor is 1.93 in place of 1.18.

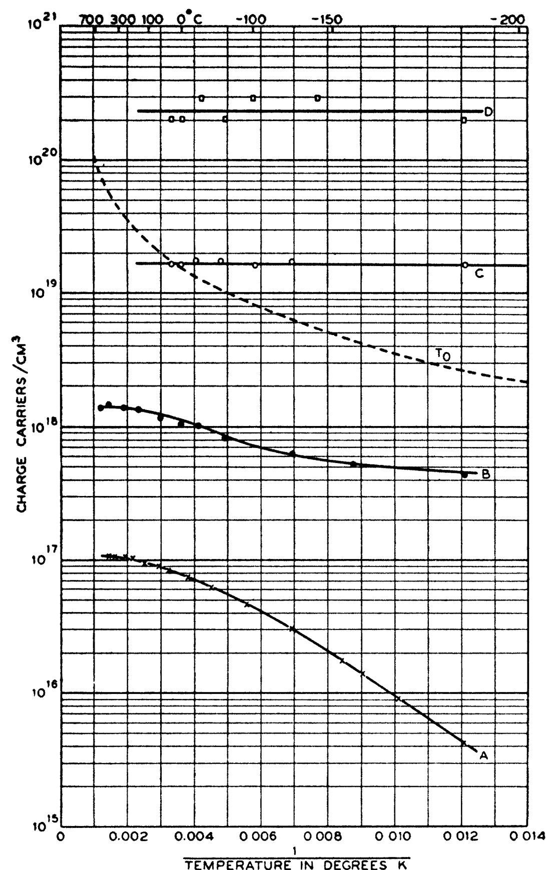


FIG. 7B. Number of charge carriers per unit volume in silicon-phosphorus alloys as a function of the inverse absolute temperature. Compositions are given in Table I. T_0 is the degeneracy temperature.

The equation relating the moboility μ, the mean free path l, and the effective mass m_e is

$$\mu=(4/3)el(2\pi m_e kT)^{-\frac{1}{2}}(\text{e.s.u.}). \qquad (12)$$

If $m_e=m$, the mass of an electron in free space,

$$\mu=2.43\times 10^9 lT^{-\frac{1}{2}}(\text{cm}^2/\text{volt-sec.}), \qquad (13)$$

$$l=4.12\times 10^{-10}\mu T^{\frac{1}{2}}\ (\text{cm}). \qquad (14)$$

Equations (12), (13), and (14) may be applied to either electron or hole mobility, provided that the proper effective mass is used.

4.2. Degenerate Electron Gas

At low temperatures and high densities the electron gas becomes degenerate, i.e., Fermi-Dirac rather than Boltzmann statistics must be

used. The limiting temperature, T_0, is that for which the energy of an electron (or hole) corresponding to the energy at the surface of the Fermi distribution is equal to kT_0. This gives

$$T_0=(h^2/8km)(3/\pi)^{\frac{2}{3}}n^{\frac{2}{3}}=4.2\times10^{-11}n^{\frac{2}{3}}. \quad (15)$$

A plot of T_0 as a function of the concentration, n, is given in Fig. 6. For $T\gg T_0$, the electron gas is non-degenerate, and Eqs. (3) to (14) applicable to Boltzmann statistics should be used. For $T\ll T_0$ the electron gas is completely degenerate, and the equations generally applied to conduction in metals may be used. Some of these are listed below. The intermediate case, for $T\sim T_0$, has been discussed by Johnson and Lark-Horovitz.[15] The equations are much more complicated than for the two limiting cases, and we will not attempt to interpret the curves in this region.

The expression for the Hall coefficient is slightly different for a degenerate electron gas in that the numerical factor is unity instead of $3\pi/8$. The basic equations are:[13]

$$\sigma=ne\mu, \quad (16)$$

$$R=\pm1/en=\pm6.25\times10^{18}/n, \quad (17)$$

$$n=\pm6.25\times10^{18}/R, \quad (18)$$

$$\mu=\pm\sigma R, \quad (19)$$

where the plus signs apply to hole conductors and the minus signs to electron conductors.

The relation between the mean free path, l, and the mobility, μ, is

$$l=(h/2e)(3n/\pi)^{\frac{1}{3}}\mu(\text{e.s.u.}). \quad (20)$$

If μ is expressed in cm²/volt-sec.,

$$l=2.02\times10^{-15}n^{\frac{1}{3}}\mu(\text{cm}). \quad (21)$$

4.3 Calaculation of n, μ, and l

Using Eqs. (5) and (18), the density of holes for the silicon-boron alloys was calculated and plotted in Fig. 7A as a function of temperature. It can be seen that n varies from 10^{14} to 5×10^{20} and is a function of temperature and boron content. The degeneracy temperature T_0 is plotted for reference in this figure. Samples 1 to 4 are non-degenerate, and log$n$ increases linearly with temperature until saturation is reached just before entering the intrinsic range. In samples 5 to 8, which are degenerate over most of the

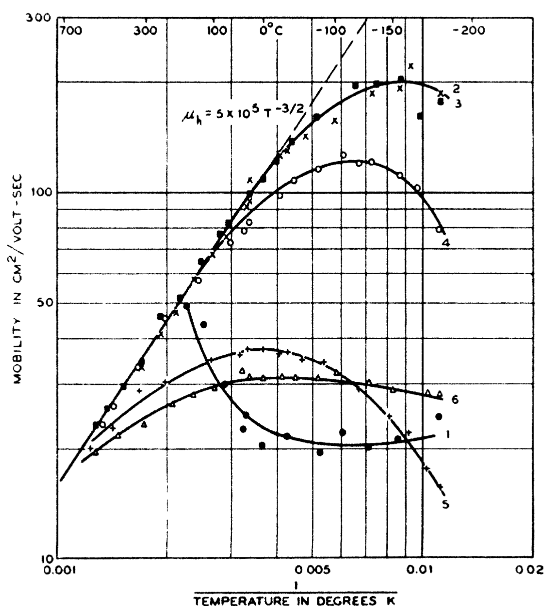


FIG. 8A. Hole mobility *versus* inverse absolute temperature for silicon-boron alloys. Compositions are given in Table I.

[15] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **71**, 374 (1947); **72**, 531A (1947).

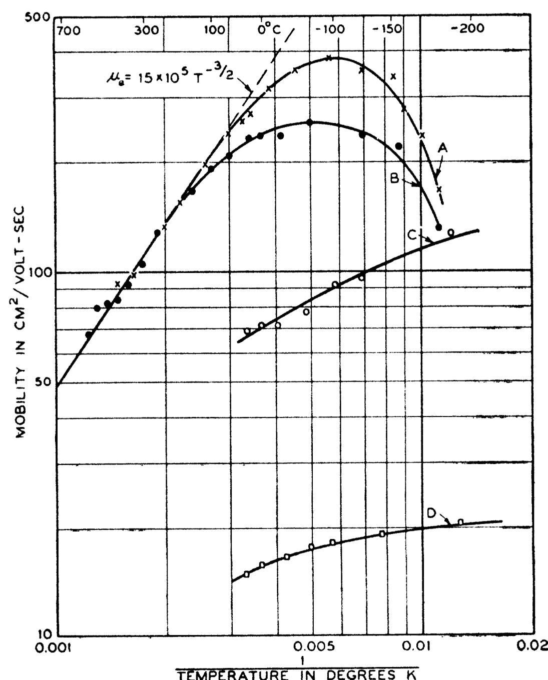


FIG. 8B. Electron mobility *versus* inverse absolute temperature for silicon-phosphorus alloys. Compositions are given in Table I.

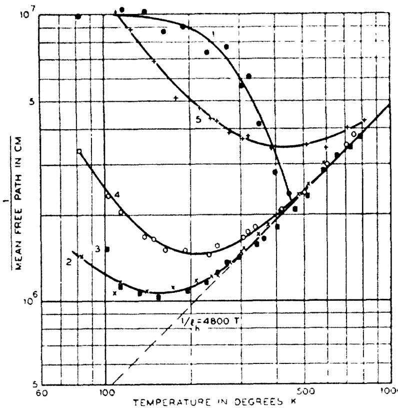


FIG. 9A. Reciprocal of the mean free path of conduction holes in silicon-boron alloys *versus* the temperature in degrees absolute. Compositions are given in Table I.

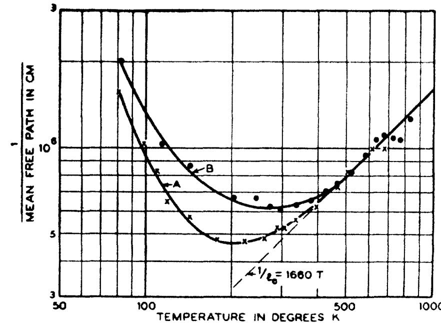


FIG. 9B. Reciprocal of the mean free path of conduction electrons in silicon-phosphorus alloys *versus* the temperature in degrees absolute. Compositions are given in Table I.

temperature range, n is approximately constant with temperature. The intrinsic line on the left was calculated by substituting the high temperature Hall data for sample No. 1 into Eq. (11) using a value $c=3.0$ as derived below.

Figure 7B gives the density of conduction electrons as a function of temperature for the silicon-phosphorus alloys as calculated from Eqs. (5) and (18). Samples A and B are non-degenerate and samples C and D degenerate.

Figure 8A gives the hole mobility μ_h in the silicon-boron alloys as a function of temperature as determined by Eqs. (6) and (19). The mobility varies between 20 and 200 cm²/volt-sec., depending on the temperature and impurity content. In the higher temperature range the curves for the different alloys join a single line which fits the equation $\mu_h = 5\times 10^5 T^{-\frac{3}{2}}$. In this temperature range, scattering by vibrations of the crystal lattice predominates. As the temperature is lowered, the mobility reaches a maximum and then decreases, the maximum value being dependent on the number of acceptor impurities present. Impurity scattering will be described in more detail in Section 6.1. Sample No. 1 does not follow the normal pattern and we believe this is due to non-homogeneity of this melt. Figure 8B gives the electron mobility μ_e in the silicon-phosphorus alloys as a function of temperature. The general pattern is similar to Fig. 8A except that the ratio of the electron to hole mobility in the lattice scattering range is about 3.

Figures 9A and 9B give the reciprocal of mean free path for holes and electrons in the silicon alloys as computed from Eqs. (14) and (21). In the lattice scattering range there is a linear inverse relationship between mean free path and absolute temperature just as found in metals. The mean free path of the electrons in the lattice scattering range is three times that of the holes. In the impurity scattering range the mean free path decreases with increasing impurity content and at a given impurity content decreases with decrease in temperature.

V. ANALYSIS OF CONCENTRATION DATA

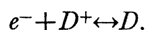
5.1. Correlation between Impurity Concentration and Charge Carrier Density

It can be seen from Figs. 7A and 7B that as the temperature is raised the concentration of holes in the silicon-boron alloys and the concentration of conduction electrons in the silicon-phosphorus alloys approach a saturation value just below the intrinsic range. This results from the fact that all acceptor or donor impurity atoms become ionized, and a further rise in temperature cannot increase the number of charge carriers until thermal energy is sufficient to raise electrons from the filled to the conduction band. By comparing the density of charge carriers in this saturation region with the density of solute atoms in the melt, one can determine the number of charge carriers supplied by each ionized impurity atom. Such a comparison is given in columns V, VI, and VII of Table I for each of the samples under study. The silicon-boron samples numbered 2 to 7 have a ratio of hole density to boron atom density close to unity,

which shows that each donor impurity atom contributes one hole. In sample 8, to which 1.3 atomic percent of boron had been added, the ratio dropped to 0.36. A microscopic examination of this melt indicated that only a part of the boron atoms went into solid solution with the remainder forming a second phase at crystalline grain boundaries. Although the ratio obtained for each of the four silicon-phosphorus melts is appreciably less than unity, we believe that each ionized donor atom produces one conduction electron and that the small ratio is due to loss of phosphorus atoms during the processing of the melt. Such a loss is to be expected since the vapor pressure of phosphorus is much higher than that of silicon. A spectroscopic analysis has verified this conclusion.

5.2 Calculation of Impurity Ionization Energies

As the equations which determine the variation of electron concentration with temperature in the impurity range of an n-type semiconductor are similar to those which give the hole concentration in p-type material, we will discuss explicitly only the case of electrons.[16] We assume that the concentrations of conduction electrons, donors, and acceptors are n_e, N_D, and N_A. In an n-type semiconductor, N_D is larger than N_A and all acceptor levels are occupied (ionized). The energy required to raise an electron from a donor level to the conduction band is E_D. The equilibrium concentration of electrons, n_e, at any temperature is determined by a balance between the rate at which electrons are thermally excited from neutral donors to the conduction band and the rate at which electrons recombine with ionized donors. The equation governing the reaction may be written



$$e^- + D^+ \leftrightarrow D.$$

The concentration of ionized donors is $N_A + n_e$, since N_A electrons go from the donor levels to ionize the acceptors and n_e to the conduction band. The concentration of neutral donors is $N_D - N_A - n_e$. The law of mass action for the reaction may be written in the form

$$n_e(n_e + N_A)/(N_D - N_A - n_e) = K_e. \quad (22)$$

The equilibrium constant, K_e, determined from statistical considerations, is

$$K_e = (2\pi m_e kT/h^2)^{\frac{3}{2}} \exp(-E_D/kT), \quad (23)$$

in which m_e is the effective mass of the electron. Equation (22) may be expressed in the form

$$(n_e + N_A)(n_e + K_e) = N_D K_e, \quad (24)$$

which is a quadratic equation for the electron concentration n_e.

If N_A is greater than N_D, the semiconductor is p-type. The same equations apply with n_h, N_A, and N_D replacing n_e, N_D, and N_A. The corresponding equilibrium constant is

$$K_h = (2\pi m_h kT/h^2)^{\frac{3}{2}} \exp(-E_A/kT), \quad (25)$$

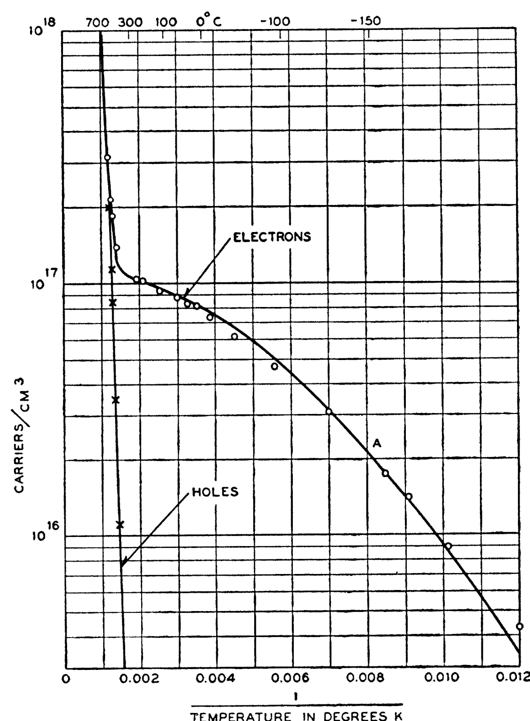


FIG. 10. Concentrations of conduction electrons and holes in sample A, Si+0.001 percent P *versus* inverse absolute temperature. Above room temperature, points are derived from resistivity using lattice scattering mobility as discussed in Section 5.3. Solid lines are derived from semi-empirical Eq. (45), using saturation concentration $N_s = 10.5 \times 10^{16}$. For fit of Hall data in this range, see Table III. Below room temperature, points are derived from Hall data, solid line from semi-empirical theory using Eq. (22), with $N_D = 12 \times 10^{16}$, $N_A = 1.5 \times 10^6$, $E_D = 0.045$ ev, and $m_e = 0.33m$.

[16] The equations to be presented in this section were first derived by J. H. de Boer and W. C. van Geel, Physica 2, 286 (1935). See N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), Chapter V.

TABLE II. Concentrations and ionization energies of donors and acceptors as determined from Hall data at low temperatures.

Sample	N_A	N_D	E_A or E_D
1— ——	15×10^{15}	9×10^{15}	0.075 ev
2—Si+0.0005%B	6×10^{17}	——	0.048 ev
3—Si+0.001%B	1.3×10^{18}	——	0.037 ev
4—Si+0.002%B	2.2×10^{18}	——	0.027 ev
5—Si+0.005%B	5.3×10^{18}	——	0
A—Si+0.001%P	1.5×10^{16}	12×10^{16}	0.045 ev
B—Si+0.0057%P	——	1.25×10^{18}	0

in which m_h is the effective mass of a hole and E_A is the energy required to excite an electron from the filled band to an acceptor level.

The saturation concentrations, attained at temperatures so high that all donors and acceptors are ionized, are

$$n_s = N_D - N_A (n\text{-type}), \tag{26a}$$

$$n_s = N_A - N_D (p\text{-type}). \tag{26b}$$

The equations which determine the concentration in the intrinsic range will be discussed in the following section.

By fitting the variation of concentration with temperature as determined from the Hall effect (see Figs. 7A and 7B) to the theoretical, the concentrations of donors and acceptors and the corresponding ionization energies have been determined. It is only for the purest samples, No. 1, "du Pont silicon," and A, "Si+0.001 percent P," that the concentrations of donors and acceptors are comparable so that both need be considered. The observed concentrations for sample No. 1 are somewhat irregular, so that the interpretation is uncertain. Values for $T<250°$K can be fitted fairly well by taking $N_A=15\times10^{15}$, $N_D=9\times10^{15}$, giving $n_s=6\times10^{15}$, together with an ionization energy, E_A, equal to 0.075 ev. The effective mass of a hole, m_h, is taken equal to the free electron value, m, in calculating K_h from Eq. (25). The best fit to the observed data for sample A was obtained with $N_D=12\times10^{16}$, $N_A=1.5\times10^{16}$, giving $n_s=10.5\times10^{16}$, together with an ionization energy for donors, E_D, equal to 0.045 ev. It was found that a better fit could be obtained by taking a value for m_e less than m, and a value $m_e=0.33m$ was adopted. This value for m_e is only about half that estimated from other considerations. Because of the number of adjustable parameters involved, these values are uncertain. A comparison of calculated and observed values of n_e is given in Fig. 10. The concentration of holes is also shown.

The remaining non-degenerate p-type samples, Nos. 2, 3, 4, and 5, contain sufficient added boron so that the concentration of acceptors is large compared with any small residual concentration of donors. Accordingly, the observed data were fitted by setting $N_A=n_s$ and $N_D=0$. Taking $m_h=m$, the only remaining parameter is the ionization energy, E_A, which was determined in each case to give the best fit. The values obtained are listed in Table II and are plotted in Fig. 11. Figure 12 gives a comparison of the theoretical and experimental values of n_h. The solid lines were calculated using the constants listed in Table II and the points are those derived from Hall measurements. The agreement is satisfactory.

There is a continuous decrease in E_A as N_A increases. Sample 5, with $N_A=6.5\times10^{18}$, exhibits relatively little change in concentration with temperature, so we have set $E_A=0$. The degeneracy temperature for this sample is about 150°K. Similarly, the variation of n_e with temperature is small at low temperatures in sample B, which is n-type with $N_D=1.25\times10^{18}$. We have set $E_D=0$ for this sample, although this may be a borderline case as n_e changes by a factor of about two between 150 and 300°K. The degeneracy temperature for this sample is about 50°K for $m_e=m$, or about 150°K if $m_e=0.33m$.

In a neutral donor, the electron moves in a hydrogen-like orbit about the ion. Similarly, in a neutral acceptor, a hole moves in a hydrogen-like

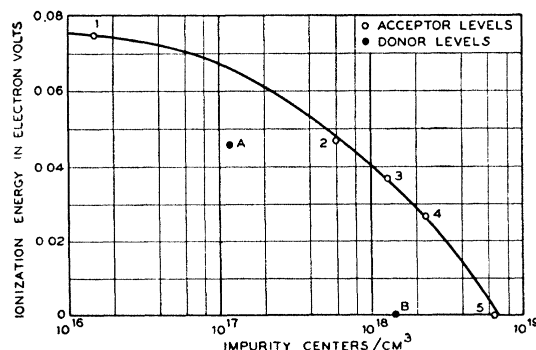


FIG. 11. Variation of ionization energy of impurity centers with concentration.

orbit about the negative acceptor ion. In each case, the force acting on the mobile charge is reduced by the dielectric constant, κ, of the medium. The ionization energy is reduced by κ^2 and the radius of the orbit is increased by κ. Since the radius of the orbit is large compared with the radius of the ion, only the Coulomb field of the ion is important in determining the energy. The ionization energy for a mass m^* and dielectric constant κ is given by the Bohr formula,

$$E_I = 2\pi^2 m^* e^4/\kappa^2 h^2. \qquad (27)$$

For the case of holes in silicon we set $m^* = m_h = m$ and $\kappa = 13$, which gives

$$E_A = 13.5/13^2 = 0.08 \text{ ev}. \qquad (28)$$

This value is close to that observed for the limit of high dilution.

The decrease in activation energy with increase in concentration probably results from a decrease in the average potential energy of an electron or of a hole.[17] If an isolated atom or impurity center is ionized, the electron is removed to infinity so that there is no resultant potential energy of attraction between the ion and the electron. In a semiconductor the conduction electrons will tend to shield the ions, so that on the average any small region of the crystal will be electrically neutral. There will be a resultant potential energy of attraction which will be greater the higher the concentration. Other things being equal, this energy will be inversely proportional to the average distance of separation between impurities, or, for the case of p-type samples, to $N_A^{1/3}$. Thus, on theoretical grounds one might expect the ionization energy to vary with concentration as

$$E_A = E_I - aN_A^{1/3}, \qquad (29)$$

where E_I is the ionization energy for an isolated impurity center, about 0.08 ev in silicon, and a is a constant.

The values of E_A determined by experiment can be fitted closely by an expression of this form. The solid line in Fig. 11 is plotted from

$$E_A = 0.08 - 4.3\times 10^{-8} N_A^{1/3} (\text{ev}). \qquad (30)$$

The value 0.08 for E_I is in agreement with Eq.

[17] For a similar suggestion, see T-W, p. 66.

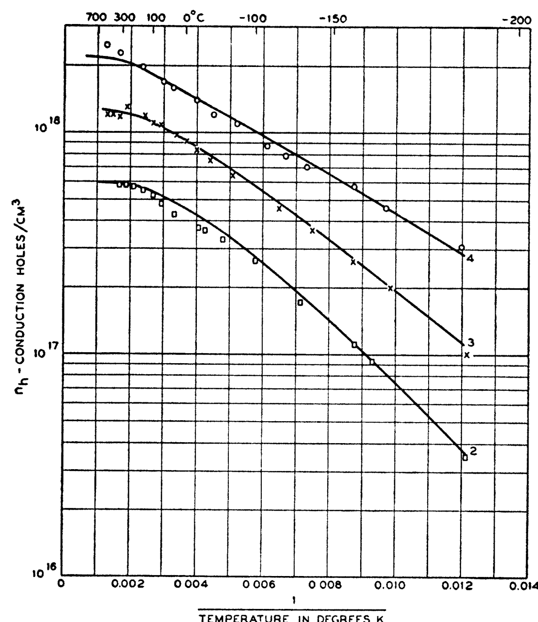


FIG. 12. Concentration of holes in samples 2, 3, and 4 *versus* inverse absolute temperature. Points are derived from Hall data, solid lines from semi-empirical theory using concentrations, and ionization energies listed in Table II.

(28). The value of a was determined by an empirical fit of the data. A theoretical discussion of the factor a is given below.

Also shown in Fig. 11 are two points, labelled A and B, which give the ionization energies for the donor levels determined from the Hall data on samples A and B. They lie below the curve for acceptors. It is probable that the effective mass of the conduction electrons is less than the free electron value, m, so that E_I is less than 0.08 ev for donors. A value

$$m_e = 0.67m \qquad (31)$$

gives

$$E_D = 0.054 \text{ ev}, \qquad (32)$$

which is in reasonable agreement with the observations.

An accurate calculation of the potential energy term is difficult. We will attempt only very rough considerations to see whether or not the empirical value is of reasonable magnitude. The impurities are probably distributed more or less at random. The mobile charges are probably distributed in such a way as to shield the ions from one another. Following the method of Wigner

TABLE III. Concentrations and Hall coefficient in intrinsic range as determined from conductivity and mobility, $\mu_e = 3\mu_h = 15\times 10^{15} T^{-\frac{3}{2}}$.

Sample	$1000/T$	μ_h	ρ	$n_e \times 10^{-17}$	$n_h \times 10^{-17}$	R(calc.)	R(obs.)
$A-Si+0.001P$	1.628	32.8	0.600	1.06	0.01	−69.5	−70
	1.472	28.0	0.620	1.16	0.11	−59	−68.5
$n_s = 1.05\times 10^{17}$	1.386	25.8	0.534	1.40	0.35	−44	−45
	1.314	23.7	0.410	1.88	0.83	−29.5	−27
	1.285	23.0	0.350	2.18	1.13	−23	−20
	1.215	21.0	0.264	3.06	2.01	−15	−14
1−du Pont Si	1.99	53.5	14.9	0.0035	0.0835	+495	+750
	1.87	44.0	14.1	0.0070	0.0870	+151	+310
$n_s = 0.08\times 10^{17}$	1.82	40.3	13.1	0.0105	0.0905	−22	−22
	1.80	38.7	12.3	0.0140	0.0940	−132	−151
	1.78	37.5	11.5	0.0162	0.0962	−178	−262
	1.75	36.5	10.2	0.0215	0.1015	−248	−400
	1.69	34.6	7.12	0.0435	0.1235	−310	−489
	1.63	32.6	4.65	0.120	0.201	−206	−434
	1.57	31.0	3.05	0.145	0.225	−183	−276
	1.51	28.7	2.00	0.252	0.332	−120	−212
	1.40	26.0	0.98	0.592	0.672	−58	−93
	1.32	23.8	0.69	0.925	1.005	−31	−43
	1.26	22.3	0.385	1.80	1.88	−20	−25
$2-Si+0.0005B$	1.34	24.8	0.408	0.07	5.97	+10.4	+8.45
	1.26	22.5	0.340	0.58	6.48	+1.4	+3.04
$n_s = 5.9\times 10^{17}$	1.12	18.8	0.164	3.60	9.50	−4.1	—

and Seitz,[18] it should be possible to draw a roughly spherical region about each ion which is electrically neutral. The average radius, r_s, of such a sphere is given by

$$4\pi r_s^3/3 = N_A^{-1}, \tag{33}$$

or

$$r_s = 0.62 N_A^{-\frac{1}{3}}. \tag{34}$$

If it is assumed that the mobile charges are uniformly distributed throughout the sphere, the potential energy of attraction is

$$-1.5e^2/\kappa r_s. \tag{35}$$

The self-energy of the uniform charge distribution in the sphere is

$$+0.6e^2/\kappa r_s. \tag{36}$$

This calculation assumes no correlations between the positions of the mobile charges. Actually, there is probably a large correlation energy resulting from the fact that these charges tend to keep apart. The most stable arrangement, which will be approached when the kinetic energy is small compared with the potential, is body-centered cubic. The reduction in potential energy relative to a random distribution is

$$-0.746e^2/\kappa r_s. \tag{37}$$

The sum of these three contributions is

$$-1.646e^2/\kappa r_s. \tag{38}$$

Substituting for r_s from Eq. (34), and putting in numerical values, this becomes

$$-3\times 10^{-8} N_A^{\frac{1}{3}} \text{ (ev)}, \tag{39}$$

which is about $\frac{2}{3}$ of the empirical value. The mobile charges may be concentrated more in the vicinity of the ions than we have assumed, increasing the energy of attraction.

If this is the correct picture, the assumption of a single ionization energy independent of the degree of ionization of the impurities can be considered to be only an approximation.

5.3. Concentrations in the Intrinsic Range

The expressions (7) and (8) for the conductivity and Hall coefficient in the intrinsic range involve four quantities, two concentrations, n_e and n_h, and two mobilities, μ_e and μ_h. As there are only two measured quantities, σ and R, additional relations are required. One may be obtained from the requirement of electrical neutrality. The difference between n_h and n_e must

[18] See reference 3, Chapters 9 and 10. The theory of a metallic modification of hydrogen, which is similar to our problem, has been discussed by E. Wigner and H. B. Huntington, J. Chem. Phys. 3, 764 (1935).

be equal to the net concentration of impurity ions, which in turn is equal to the saturation concentration, n_s, in the impurity range. Thus

$$n_s = n_e - n_h \ (n\text{-type}), \qquad (40a)$$

$$n_s = n_h - n_e \ (p\text{-type}). \qquad (40b)$$

At high temperatures the mobilities of electrons and holes in all samples approach the values corresponding to lattice scattering, which are approximately

$$\mu_e = 15\times 10^5 T^{-\frac{3}{2}} (\text{cm}^2/\text{volt sec.}), \qquad (41a)$$

$$\mu_h = 5\times 10^5 T^{-\frac{3}{2}}. \qquad (41b)$$

The mobilities of holes in samples 2, 3, and 4 and of electrons in sample B lie on the lattice scattering line over the same temperature range for which the conductivity of samples 1 and A become intrinsic. Thus there is every reason to believe that the lattice scattering mobilities will apply in the intrinsic range.

Assuming Eqs. (41a) and (41b) for the mobilities, and using Eqs. (40a) and (40b) expressing electrical neutrality, the concentrations n_e and n_h in the intrinsic range can be found from either the conductivity or the Hall coefficient. We have determined n_e and n_h from the conductivity and used these values to calculate the Hall coefficient to compare with the observed. The conductivity may be expressed in the form

$$\sigma = e\mu_h(cn_e + n_h). \qquad (42)$$

For a p-type sample we set $n_e = n_h - n_s$ and find

$$n_h = ((\sigma/e\mu_h) + cn_s)/(c+1). \qquad (43)$$

For an n-type sample, we set $n_e = n_h + n_s$ and find

$$n_h = ((\sigma/e\mu_h) - cn_s)/(c+1). \qquad (43a)$$

Using these equations, both n_e and n_h were determined in the intrinsic range for samples 1, 2, and A. The values are listed in Table III.

Statistical theory indicates that the product of the electron and hole concentrations at any temperature is independent of impurity concentration and is given by:[19]

$$n_e h_h = 4(2\pi mkT/h^2)^3 (m_e m_h/m^2)^{\frac{3}{2}} \exp(-E_G/kT)$$
$$= 2.4\times 10^{31}(m_e m_h/m^2)^{\frac{3}{2}} T^3 \times \exp(-E_G/kT). \qquad (44)$$

A plot of $\log(n_e n_h/T^3)$ *versus* $1/T$ should then give a straight line. Such a plot is shown in Fig. 13. Values of $n_e n_h/T^3$ calculated from the values of n_e and n_h determined as above for the three samples all lie on the same straight line whose equation is:

$$n_e n_h/T^3 = 7.8\times 10^{32} \exp(-12{,}900/T). \qquad (45)$$

This equation is of the correct form, but the numerical factor is considerably larger than the theoretical. The difference seems too large to account for by the term involving the effective mass. In fact, the mass term operates in the wrong direction, as the evidence is that m_e is only about two-thirds of m. Neglecting the difference in effective mass, the discrepancy is a factor of about 32.5. It is most likely accounted for by a variation of E_G with temperature. If there is

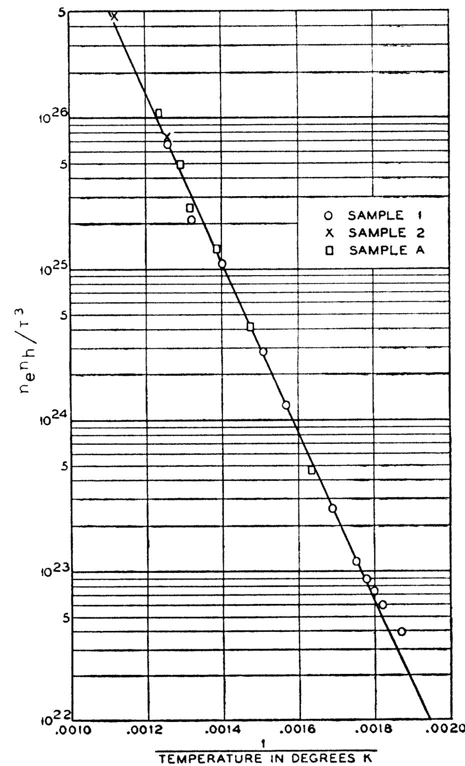


FIG. 13. Plot of $n_e n_h/T^3$ *versus* inverse absolute temperature for samples 1, 2, and A. Equation of straight line is $n_e n_h/T^3 = 7.8\times 10^{32} \exp(12{,}900/T)$.

[19] See, for example, R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, London, 1936), second edition, Chapter 11. While not given explicitly, Eq. (44) can be derived readily from the relations expressing n_e and n_h in terms of the Fermi level.

TABLE IV. Fit of mobility data by $1/\mu = aT^{-3/2} + bT^{3/2}$.

Sample	Impurity centers/cm^3	$1.8\times 10^{-18}N_I$	a	b
$2-\mathrm{Si}+0.0005B$	0.6×10^{18}	1.1	3.1	2×10^{-6}
$3-\mathrm{Si}+0.001B$	1.3×10^{18}	2.3	3.1	2×10^{-6}
$4-\mathrm{Si}+0.002B$	2.5×10^{18}	4.5	8.3	2×10^{-6}
$A-\mathrm{Si}+0.001P$	1.0×10^{17}	0.19	3.1	0.67×10^{-6}
$B-\mathrm{Si}+0.0057P$	1.25×10^{18}	2.3	5.5	0.67×10^{-6}

linear variation, we may write

$$E_G(T) = E_G(0) - \beta T. \tag{46}$$

The empirical equation for $n_e n_h/T^3$ can be brought into agreement with the theoretical by taking

$$E_G(0) = 12{,}900/11{,}600 = 1.115 \text{ ev}, \tag{47}$$

and

$$\beta = k \log 32.5 = 3.0\times 10^{-4} \text{ ev/degree}. \tag{48}$$

The value of $E_G(0)$ is in close agreement with photoelectric studies of a silicon $p-n$ junction at low temperatures.[20] These studies also indicate a shift in response corresponding to a change in $E_G = 0.1$ ev between 90°K and 290°K, a range of 200°K, giving $\beta = 5\times 10^{-4}$. The difference between this value of β, obtained at low temperatures, and ours may be accounted for, in part, by the effective mass term.

In the limit of high temperatures, the concentration may be found by setting $n_e = n_h = n$ in Eq. (45) and solving for n. Using Eqs. (41a) and (41b) for the mobilities, the conductivity may be found for Eq. (9). The corresponding equation for the resistivity in the intrinsic range is

$$\rho = 1.1\times 10^{-4} \exp(6450/T) \text{ ohm}.$$

Values of the Hall coefficient, R, were calculated with use of the values of n_e and n_h determined from the conductivity. The calculated values are compared with the observed values in Table III. Good agreement is obtained for the n-type sample (A), but there are discrepancies for the p-type samples, (1) and (2), which appear to be outside the limits of experimental error. Agreement can be obtained by using a value of $c = 3.75$ instead of the value 3.0 obtained from the ratio of the mobilities in the sub-intrinsic range of other samples. This would correspond to an electron mobility of about $19\times 10^5 T^{3/2}$ for the intrinsic range of p-type samples as compared with $15\times 10^5 T^{-3/2}$ for electrons in n-type samples. A real difference of this sort would be surprising. If the higher value is used to compute n_e and n_h for the p-type samples, it is found that values of $n_e n_h/T^3$ for the different samples do not lie on the same line. It is possible that the theory for the Hall coefficient in the intrinsic range requires modification.

VI. LATTICE AND IMPURITY SCATTERING: ANALYSIS OF MOBILITY DATA

6.1. Lattice Scattering

We have seen that the mobilities of electrons and holes in all samples approach the same limiting curves at high temperatures, independent of impurity concentration. The mobility in this temperature range is determined by scattering by vibrations of the crystal lattice. It has been shown by Wilson,[21] and later more generally by Seitz,[22] that in a non-polar material such as germanium or silicon the mean free path is independent of velocity. Above a few degrees absolute, the scattering by lattice vibrations is isotropic, and energy is conserved during collisions. The mean free path varies as T^{-1} and in the non-degenerate case the mobility varies as $T^{-3/2}$. These theoretical predictions agree well with the experimental results for silicon, and, as pointed out by Seitz,[22] the observed values are of the expected order of magnitude.

The difference in electron and hole mobility (Eqs. (41a) and (41b)), a factor of three, may result at least in part from the fact that the effective mass of a conduction electron is less than that of a hole. Theory indicates that the mobility varies as $(m_{\mathrm{eff.}})^{-5/2}$. A factor of three would require that

$$(m_h/m_e)^{5/2} = 3,$$

or

$$m_e/m_h = 0.65. \tag{49}$$

This ratio is about the same as that required to explain the difference in ionization energies between donors and acceptors, but is about

[20] F. S. Goucher, H. B. Briggs, G. L. Pearson and W. Shockley, "Photoelectric and electric studies of $P-N$ junctions in silicon and germanium," to be published in Phys. Rev.

[21] A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1936), p. 211.

[22] F. Seitz, Phys. Rev. **73**, 549 (1948).

twice as large as that derived in Section 5.1 from concentration data for sample A. The larger value is probably more nearly correct.

6.2 Impurity Scattering—Non-Degenerate

At lower temperatures impurities contribute to the scattering, so that the mobilities are higher in the purer samples. The impurity centers which give the largest scattering are the donors and acceptors. Scattering by both ionized and neutral centers is large at low temperatures. It is not possible to make anything like an exact calculation of the way the mobility should change with temperature when both lattice and impurity scattering is involved for the following reasons:

(1) The theory of the scattering, particularly by neutral centers, is complicated, and only rough approximations are available.

(2) Scattering by the lattice, ionized centers, and neutral centers are not additive because they depend in different ways on the velocities of the carriers.[23]

In this section we attempt to give only a brief outline of theoretical considerations involved in impurity scattering, and to indicate roughly the correlation between theory and experiment. We discuss first the case of a non-degenerate gas and then the degenerate case.

Conwell and Weisskopf[24] have given an expression for the resistivity of a semiconductor which is based on scattering by ions which are present with a total concentration N_I. The expression for the reciprocal of the mobility, which applies for a non-degenerate gas, may be written in the form

$$1/\mu=(N_I\pi^{3/2}e^3m^{1/2})/(2^{7/2}\kappa^2(kT)^{3/2}) \times\log(1+x^2)\text{(e.s.u.)}, \quad (50)$$

where

$$x=6\kappa dkT/e^2. \quad (51)$$

In these equations d is the average distance the field of any one ion extends, so that $2d$ is something like the average distance between near neighbors. For the purpose of numerical calculation, we take

$$d=0.5N_I^{-\frac{1}{3}}. \quad (52)$$

The choice of the numerical factor is somewhat arbitrary. Inserting numerical values for the fundamental constants and converting to practical units, Eqs. (50) and (51) may be written for application to silicon in the form

$$1/\mu=1.8\times10^{-18}N_IT^{-\frac{3}{2}}\log(1+x^2), \quad (53)$$

$$x=2.3\times10^4N^{-\frac{1}{3}}T. \quad (54)$$

A neutral donor or acceptor consists of an electron or hole moving in a hydrogen-like orbit about the corresponding ion. The calculation of the scattering by such a center is mathematically the same as that of the scattering of an electron by a hydrogen atom, which problem has been treated theoretically by Massey and Mohr.[25] An exact calculation is difficult, particularly for incident energies less than the ionization energy, for which exchange effects are important. In the limit of zero velocity of the incident particle, the cross section for scattering is 124 times that of the Bohr orbit. The cross section decreases rapidly with increasing velocity, but is still large when the kinetic energy of the incident particle is less than about 25 percent of the kinetic energy of an electron in a Bohr orbit. The radius of the orbit about an ion in a semiconductor is increased by the dielectric constant and the cross section by the square of the dielectric constant.

To compare the scattering by neutral and ionized centers, we write down an expression for the mobility in a semiconductor containing N_n neutral scattering centers. The reciprocal of the mobility is related to the effective scattering cross section, A, by

$$1/\mu=(m/e)N_nvA \text{ (e.s.u.)}, \quad (55)$$

where v is an average thermal velocity for the carrier. We may set

$$A=124\pi\kappa^2A_0{}^2\alpha(T), \quad (56)$$

where $\alpha(T)$ is a numerical factor which equals unity at $T=0$ and decreases with increasing

[23] W. Shockley (unpublished) has made calculations of the resistivity when both lattice scattering, with l_L independent of velocity, and scattering by ions, with $l_I\sim v^{-4}$, are present. Large deviations from simple additivity are found.

[24] E. Conwell and V. F. Weisskopf, Phys. Rev. **69**, 258A (1946). The problem is mathematically identical with that of the scattering of electrons in an ionized gas which has been solved to the same approximation by S. Chapman, Monthly Notices, R.A.S. **82**, 294 (1922).

[25] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A132**, 605 (1931); **A136**, 289 (1932).

TABLE V. Limiting low temperature resistivities and mobilities for degenerate samples.

Sample	n	μ	ρ	$1.87\times10^{17}/n$
$6-\mathrm{Si}+0.01B$	1.4×10^{19}	31	1.25×10^{-2}	1.33×10^{-2}
$7-\mathrm{Si}+0.1B$	1.2×10^{20}	30	1.62×10^{-3}	1.56×10^{-3}
$8-\mathrm{Si}+1.0B$	4.8×10^{20}	54	2.21×10^{-4}	3.9×10^{-4}
$C-\mathrm{Si}+0.1P$	1.7×10^{19}	130	2.5×10^{-3}	1.1×10^{-3}
$D-\mathrm{Si}+1.0P$	2.6×10^{20}	50	5.0×10^{-4}	7.2×10^{-4}

temperature. Putting $\kappa=13$ for silicon, substituting in Eq. (55), and converting to practical units gives

$$1/\mu=7.6\times10^{-22}N_nT^{\frac{1}{2}}\alpha(T). \qquad (57)$$

This equation may be compared with Eq. (53) which applies to ionized centers. The effective scattering cross sections will be equal for a temperature such that

$$T^2=2.4\times10^3\log(1+x^2)/\alpha(T).$$

It is not unreasonable to expect that the effective scattering cross section for neutral centers is as large or is larger than the cross section for ionized centers at temperatures above about 100°K.

The mobilities of the p-type samples are shown in Fig. 8A and the n-type in Fig. 8B. Of the p-type samples, numbers 1, 2, 3, and 4 are non-degenerate and number 5 is borderline, as the degeneracy temperature is about 150°K. The mobility values for sample 1 are anomalously low. It is thought that in this case the sample is not homogeneous so that the method does not give reliable results. The mobilities of the remaining p-type samples, numbers 2, 3, and 4, and of the n-type samples, A and B, can be approximated over the temperature range by an expression of the form

$$1/\mu=aT^{-\frac{3}{2}}+bT^{\frac{3}{2}}. \qquad (58)$$

This form is suggested by assuming additivity of lattice and impurity scattering, and by the form of Eq. (53) for impurity scattering. The first term represents impurity scattering and the second term lattice scattering. The coefficient b is equal to 2×10^{-6} for the p-type samples and to 0.67×10^{-6} for the n-type samples. Values of a which give the best fit to the observed data are listed in Table IV.

The empirical values of a are of the same order as expected from theory. Equation (53) gives

$$a=1.8\times10^{-18}N_I\log(1+x^2). \qquad (59)$$

The factor multiplying the logarithm is listed in Table IV for the different samples. The logarithm is slowly varying with concentration and temperature, and may be expected to increase a by a small factor. The order of magnitude is about the same as the observed. Actually, a large fraction of the impurity centers are neutral over the temperature range, the concentration of ions decreasing with decrease in temperature, so that the comparison is not significant except as to general order of magnitude. The empirical values of a do not decrease as rapidly as expected with decreasing concentration. The discrepancy is particularly large for sample A.

6.3. Impurity Scattering—Degenerate

In the degenerate cases, the concentrations and resistivities approach constant values at low temperatures. The resistivity is determined by impurity scattering. Because of Fermi-Dirac statistics, the effective velocities of the carriers and thus the mobilities and resistivities become temperature independent. The constancy of ρ and R over a wide temperature range for samples 6, 7, 8, and D is striking.[26]

When degeneracy applies, it may be assumed that there are impurity centers of only one type and that these are all ionized. The concentration of ions is then equal to that of the electrons (or holes). Johnson and Lark-Horovitz[15] have extended the calculations of Conwell and Weisskopf to cover this case. the problem is mathematically identical with that of the calculation of the resistivity of dilute solutions of metals of higher valency in monovalent solvents such as Cu, Ag, and Au. This latter problem has been discussed by Mott.[27] He assumes that the impurity ions are screened by the electrons, so that the poten-

[26] G. L. Pearson and W. Shockley (reference 1) have found that the resistivity and Hall coefficient of a sample of silicon similar in composition to sample 6 remain constant to 10°K. Similar results were obtained for a germanium sample with added impurities. I. Esterman, A. Foner, and J. A. Randall [Phys. Rev. **72**, 530A (1947)] have reported that the resistivity and Hall coefficient of a sample of germanium with 0.04 atomic percent Al added remained substantially constant between 20°K and 200°K.

[27] N. F. Mott, Proc. Camb. Phil. Soc. **32**, 281 (1936).

tial of an ion is of the form

$$V(r) = (Ze^2/r)e^{-qr}, \quad (60)$$

where Z is the difference in valency between the solute and solvent atoms, and q depends on the screening. To apply to our case we replace Z by $1/\kappa$, where κ is the dielectric constant.

Both Mott's theory and that of Johnson and Lark-Horovitz lead to an expression for the reciprocal of the mobility of the form:

$$1/\mu = (8\pi e^2 m^2/3\kappa^2 h^3) f(y) \text{ (e.s.u.)}. \quad (61)$$

The parameter y is a measure of the ratio of the kinetic energy of an electron at the surface of the Fermi distribution, E_0, to the potential energy in the field of the ion:

$$y = \kappa E_0/e^2 n^{\frac{1}{3}} = (\kappa h^2/8me^2)(3/\pi)^{\frac{2}{3}} n^{\frac{1}{3}}. \quad (62)$$

The form of the function $f(y)$ is discussed below. Putting in numerical values for silicon gives

$$y = 3.4 \times 10^{-7} n^{\frac{1}{3}}. \quad (63)$$

Inserting constants for silicon into Eq. (61) and converting to practical units gives

$$\rho = 1/ne\mu = (1.87 \times 10^{17}/n) f(y) \text{ (ohm cm)}. \quad (64)$$

The function $f(y)$ depends on what is assumed for the field of an ion. Johnson and Lark-Horovitz assume a cut-off distance

$$d = n^{-\frac{1}{3}}/2\pi^{\frac{1}{2}} = 0.28 n^{-\frac{1}{3}}, \quad (65)$$

which, using an extension of the Conwell-Weisskopf theory, gives

$$f(y) = \log(1 + y^2/\pi). \quad (66)$$

In the limiting case of y^2 small compared with unity, the logarithm can be replaced by y^2/π, giving

$$1/\mu = (\pi h/4e)(3/\pi)^{\frac{1}{3}} n^{\frac{2}{3}} \text{ (e.s.u.)}. \quad (67)$$

The mobility and thus the resistivity are in this approximation independent of the dielectric constant and effective mass, and so should depend only on the concentration. The resistivity is inversely proportional to the cube root of the concentration. In practical units

$$\rho = 6270 n^{-\frac{1}{3}} \text{ (ohm cm)}. \quad (68)$$

This is the formula as given by Johnson and Lark-Horovitz.

Mott's expression for $f(y)$ may be written in the form

$$f(y) = \log(1 + ay) - ay/(1 + ay). \quad (69)$$

The numerical factor a is inversely proportional to the square of the screening constant, q, and is equal to $2(\pi/3)^{\frac{1}{3}}$ if the Thomas-Fermi method is used to evaluate q. Mott believes that this method yields a value for q which is too large. The best value for a may therefore be several times larger than $2(\pi/3)^{\frac{1}{3}}$. In the derivation of Eq. (69) the Born approximation is used to determine the collision cross sections. This approximation is valid in the limit of large ratios of kinetic to potential energy, that is, for large values of y. This condition is not well satisfied in our case, and it is probable that the actual cross sections are larger than given by the formula.

We would expect a formula based on screening to be more accurate than one based on a cut-off distance for the ion field, so that Mott's formula is to be preferred. The use of the Born approximation limits the accuracy that can be attained.

The experimental results do not agree well with either formula except as to order of magnitude. In Table V we have listed the limiting resistivities and mobilities and have also listed the values of the factor multiplying $f(y)$ in Eq. (64). It can be seen that these values are in fair agreement with the observed values of ρ, indicating that $f(y) \sim 1$. Both Lark-Horovitz's and Mott's expressions yield values for $f(y)$ which are smaller than unity. It appears likely, however, that appropriate modifications of Mott's theory would yield agreement.

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