Properties of Silicon and Germanium*

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Summary—This article provides the latest experimental information on those fundamental properties of germanium and silicon which are of device interest, currently or potentially. Electrical properties, especially carrier density and mobility, have been treated in greatest detail. Descriptive material has been provided to the extent necessary to give physical background.

INTRODUCTION

IN THIS ARTICLE it is proposed to present the latest available information on the properties of germanium and silicon and, in particular, the best experimental values for important physical quantities. It need scarcely be mentioned that in a field which is developing as rapidly as this some of the information will be obsolete shortly. The general state of development is such, however, that major changes are not anticipated.

It is assumed that the reader is familiar with the elements of the band description of semiconductors to the extent that these are covered in the article by Shockley in this issue[1] or in chapter I of "Electrons and Holes in Semiconductors."[2] For most purposes in this article electrons in the conduction band can be thought of as negatively charged particles moving with random thermal energy through the crystal, differing only from a free electron gas in that the free electron mass is replaced by the appropriate effective mass. Similarly, holes in the valence band can be thought of as free positively charged particles with a different effective mass. In each case the effective mass is the same order of magnitude as the free electron mass.

Electrical properties have been taken up first. Since conductivity depends on the density of current carriers and their mobility, both of which are more fundamental, sections on these precede the section on conductivity. Magnetic, optical, thermal, and mechanical properties have been presented in much less detail than the others because they are currently of less device interest. As is necessary to supplement this type of survey, extensive references have been given. No attempt has been made, however, to provide a complete bibliography.

DENSITY OF CURRENT CARRIERS

A pure, perfect crystal of germanium or silicon at the absolute zero of temperature would have no electrons in the conduction band and no holes in the valence band. The current carriers present at higher temperatures originate in the valence band, chemical impurities in

the lattice, and lattice defects of some types. Of primary importance in determining the number of carriers that each source supplies under a given set of external conditions is its ionization energy, i.e., the energy required to liberate a bound electron or hole. This will now be considered for each of the three in the order stated.

To raise an electron from the valence band to the conduction band, creating a hole-electron pair, requires energy equal to the energy gap between these bands. Since the electron energy levels depend on the spacing between atoms, the energy gap would be expected to depend somewhat on temperature and pressure. The energy gap has been found to depend linearly on temperature according to

$$\epsilon_G(T) = \epsilon_G(0) - \beta T, \tag{1}$$

where $\epsilon_G(T)$ represents the value of the energy gap at the absolute temperature T and β is a constant. The values of these quantities found empirically are listed in Table I.[3]

TABLE I

SOURCE OF CARRIERS	IONIZATION ENERGY IN ELECTRON VOLTS	
	GERMANIUM	SILICON
Valence band	$0.75 - .0001T^4$	$1.12 - .0003T^5$
B, Al, Ga, In (Low concentration)	$0.01 - ^4$	0.08^5
P, As, Sb (Low concentration)	$0.01 + ^6$	0.05^5
Zn (Low concentration)	0.03^7	
Thermal acceptors (Cu)	0.03^8	

[4] J. Bardeen and W. Shockley, *op. cit.* Note, however, that optical experiments given $\epsilon_G(0) = 0.72$ ev. See footnotes for discussion of the precision of the temperature coefficients for germanium and silicon.
[5] G. L. Pearson and J. Bardeen. *loc. cit.*
[6] P. P. Debye, private communication, Bell Telephone Laboratories, Inc., the slope of $\log_e nT^{-3/2}$ versus $1/T$, and are therefore only approximately equal to the ionization energy. For a discussion of this point, see W. Shockley, *op. cit.*, p. 471. The quoted values are, however, Boltzmann's constant times.
[7] W. C. Dunlap, Jr., "Zinc as an acceptor in germanium," *Phys. Rev.*, vol. 85, p. 1945; 195a. Also, P. P. Deby, private communication, Bell Telephone Laboratories Inc., Murray Hill, N. J. Again this value is approximate for the reasons discussed in footnote reference 14.
[8] W. DeSorbo and W. C. Dunlap, Jr., "Resistivity of heat-treated germanium between 11°K and 298°K," *Phys. Rev.*, vol. 83, pp. 869, 879; 1951.

In both silicon and germanium the energy gap increases when pressure is applied. The temperature dependence of the energy gap can be used to compute its pressure dependence if the assumption is made that the change of energy gap with temperature is due entirely to thermal expansion.[9] The changes in energy gap per unit dilation computed from the values of β given in Table I are 3×10^1 and 5 ev per unit dilation for silicon

[1] W. Shockley, "Transistor electronics: imperfections, unipolar and analog transistors," PROC. I.R.E., vol. 40, pp. 1289–1314; this issue.
[2] W. Shockley, "Electrons and Holes in Semiconductors," D. Van Nostrand Co., Inc., New York, N. Y.; 1950.

[3] The stated values of β, however, are in considerable doubt because they involve the assumption that the effective mass of an electron or hole is equal to the free electron mass. This can be only approximately true. See formula (2) and associated text and footnote.
[9] See, however, footnote reference 20(a) in J. Bardeen and W. Shockley, "Deformation potentials and mobilities in nonpolar crystals," *Phys. Rev.*, vol. 80, pp. 72–80; 1950.

and germanium, respectively. Approximately the latter value has been obtained for germanium by a number of experiments of other types as well.[10]

Chemical impurities in the lattice may act as donors or acceptors. Those which have been studied extensively are elements in column III of the periodic chart, which act as acceptors, e.g., boron, aluminum, gallium, and indium, and elements in column V, which act as donors, e.g., arsenic, phosphorus, and antimony. Since the electron or hole is bound loosely in a large hydrogen-like orbit, it is expected that the ionization energy should be about the same for all these elements, and this is in fact found. This ionization energy decreases with increasing impurity concentration, vanishing for concentrations of about 10^{18} or $10^{19}/cm^3$. The values stated in Table I are for small impurity concentration, up to about $10^{15}/cm^3$ perhaps.[11] Zinc, which has also been studied, acts as an acceptor with considerably greater ionization energy than the elements of columns III and V. This value is also listed in Table I.

It has been found that acceptors can be introduced in germanium by means of heat treatment at temperatures above about 600°C.[12] Equilibrium concentration of acceptors introduced for a given temperature of heat treatment increases exponentially with the temperature over a considerable range. With this process it is possible to convert n-type germanium into p-type provided the initial n-type resistivity is not too low. Prolonged heating at 500°C is found to reverse this conversion. The process is also characterized by diffusion of the acceptors from the surface into the interior at a rate which is large for diffusion in solids.[13] The ionization energy for these thermal acceptors has been measured and is listed in Table I. There has been considerable speculation about the nature of these acceptors. The effects described might, in principle, arise from the introduction by the heat treatment of either lattice defects[14] or chemical impurities. It has recently been established, however, that copper is one important agent, if not the sole agent, responsible for these phenomena. In one set of experiments it was found that germanium which was heat treated for several hours in a hydrogen atmosphere and in a system free from contaminants was not converted, whereas it was if copper were added.[15]

[10] For a discussion of, see J. Bardeen and W. Shockley, op. cit.

[11] For a study of the variation with impurity content in silicon, see G. L. Pearson and J. Bardeen, "Electrical properties of pure silicon and silicon alloys containing boron and phosphorus," *Phys. Rev.*, vol. 75, pp. 865–883; 1949.

[12] J. H. Scaff and H. C. Theuerer, "Effect of heat treatment on the electrical properties of germanium," *Jour. Met.*, vol. 191, pp. 59–63; 1951.

[13] C. S. Fuller, H. C. Theuerer, and W. van Roosbroeck, "Properties of thermally produced acceptors in germanium," *Phys. Rev.*, vol. 85, pp. 678–679; 1952.

[14] Evidence that disorder in the lattice produces acceptors and donors is provided by experiments in which germanium and silicon are bombarded by high-speed atomic particles. See the chapter entitled "Nucleon Bombarded Semiconductors," by K. Lark-Horovitz in "Semiconducting Materials," Butterworth's Scientific Publications Ltd., London; 1951.

[15] W. P. Slichter and E. D. Kolb, "Impurity effects in the thermal conversion of germanium," *Phys. Rev.*, vol. 87, pp. 527–528; August 1, 1952.

Furthermore, experiments with radioactive copper indicate that the diffusion rate and equilibrium concentration of copper in germanium are, within experimental error, the same as those measured for the thermal acceptors.[16] It has also been shown that copper acts as an acceptor in the germanium lattice.

The energy required to ionize a donor or acceptor can be supplied in a number of ways, the most usual being heat and light. Strong electric fields can also create hole-electron pairs. This is called the "Zener effect" and will be discussed later under that heading. The effect of light will be considered in the section on optical properties. The remainder of this section will be devoted to considering the variation of carrier density with temperature.

Theory indicates that for a specimen in thermal equilibrium the product of the electron concentration, denoted by n, and the hole concentration, denoted by p, is a function of temperature only, given by

$$np = 2.33 \times 10^{31} \left(\frac{m_n m_p}{m^2} \right)^{3/2} T^3 e^{-\epsilon_G/kT}, \qquad (2)$$

where m_n and m_p denote the effective masses of electrons and holes, respectively, m is the free electron mass, and k is Boltzmann's constant. The values found empirically are listed in Table II. When the number of carriers donated by impurities or lattice defects is small compared to the number from the valence band of the semiconductor, the conduction is called "intrinsic." In that case,

$$n \simeq p = n_i \qquad \text{intrinsic conduction.} \qquad (3)$$

This enables the use of (2) or, speaking practically, of the empirical formulas of Table II[17] to compute the density of electrons or holes in intrinsic material at any temperature. The results are

$$n_i = 9.7 \times 10^{15} \ T^{3/2} e^{-4350/T} \ \text{Ge},$$
$$n_i = 2.8 \times 10^{16} \ T^{3/2} e^{-6450/T} \ \text{Si}. \qquad (4)$$

The values of n_i for 300°K are listed in Table II. In Fig. 1 n_i is plotted as a function of temperature. In the temperature range where the conduction is not intrinsic, (2) still holds for a specimen in thermal equilibrium, but the densities of electrons and holes, respectively, depend on the concentrations of donors and acceptors and the ionization energy in a relatively complicated fashion. There are two practical procedures for determining n and p for a given extrinsic sample at a given temperature. One way involves measuring the resistivity. This is related to np and the mobilities of electrons and holes according to formula (8). (See section on conductivity.) The mobilities can be computed as

[16] C. S. Fuller and J. D. Struthers, "Copper as an acceptor element in germanium," *Phys. Rev.*, vol. 87, pp. 526–527; August 1, 1952.

[17] Since the effective masses are not known (with one exception) but are probably not very different from the free electron mass, it is customary to set the factor in (2) involving the masses equal to 1. The empirical value of np is then compared with (2) to obtain the values of β and E_G (0) listed in Table I.

TABLE II

	VALUE	
QUANTITY	GERMANIUM	SILICON
Electron density × hole density	$9.3 \times 10^{31} T^3 e^{-8700/T}$ per cm⁶ [18]	$7.8 \times 10^{32} T^3 e^{-12,900/T}$ per cm⁶ [18]
Density of carriers in intrinsic material at 300°K	2.5×10^{13}/cm³	6.8×10^{10}/cm³
Intrinsic resistivity at 300°K	47 ohm cm	63,600 ohm cm

[18] W. van Roosbroeck, private communication, Bell Telephone Laboratories, Inc., Murray Hill, N. J.

described in the next section. With numerical values for ρ, e, μ_n, and μ_p inserted in (8) it provides a relationship between n and p which can be used in conjunction with the empirical formula for np in Table II to determine these quantities. A second and more direct procedure to determine them is by measuring the Hall effect.[19]
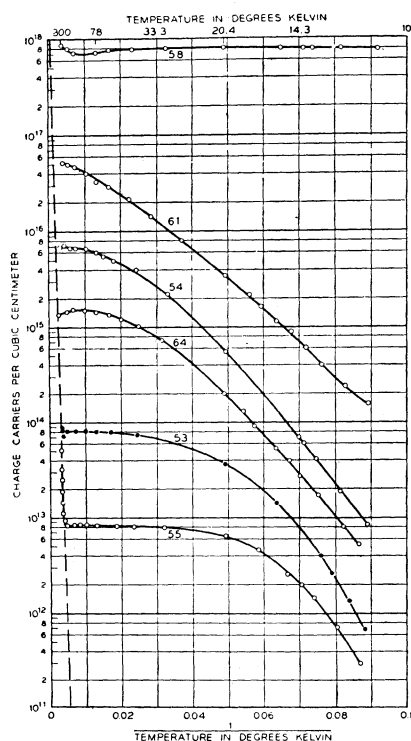

Fig. 1—Density of charge carriers versus the reciprocal of absolute temperature for a set of arsenic-doped germanium samples. The data were taken by Debye at Bell Laboratories. The numbers identify particular samples. The dashed line represents the density of intrinsic carriers.

Since the variation of carrier concentration with temperature for an extrinsic sample is not given here explicitly, it is useful to illustrate this for some particular cases. For this purpose there are shown in Fig. 1 experimental data for a set of n-type germanium samples with increasing amounts of arsenic (donor) impurity. These have been chosen to represent all parts of the resistivity range. Sample 55 is very pure, with a room-temperature resistivity of about 40 ohms cm, while sample 58 at the other end of the resistivity spectrum is 0.005 ohm cm. (Mobility and conductivity are plotted for these same

[19] See W. Shockley, *op. cit.*, p. 204.

samples in Figs. 4 and 6, respectively.) Sample 58 has essentially the same number of carriers at all temperatures, or zero ionization energy. For all others, carrier concentration is relatively small at low temperatures, but increases rapidly with temperature because of the small ionization energy of the donors. For the pure and moderately impure ones, essentially all the electrons are freed from the donors somewhat below room temperature. The density then remains constant with increasing temperature[20] until temperatures are reached so that a substantial number of electrons in the valence band receive sufficient energy for the valence bonds to be broken, i.e., until the sample starts to become intrinsic. At temperatures higher than this the number of carriers is just the intrinsic number and is given by the dashed line.

For germanium doped with a column III impurity, i.e., p-type, the variation of carrier concentration with temperature would be very much the same. In the case of silicon the curves would be of this general type, but because of the higher ionization energy not all the electrons or holes would be free at room temperature. Also, because of the larger energy gap silicon would not become intrinsic until higher temperatures.

MOBILITY

Low Field Case

In the absence of an electric field, electrons and holes move in the crystal with random thermal energy. Their speeds will be distributed according to a Maxwell-Boltzmann distribution, with the average speed therefore proportional to $\sqrt{T}$. Application of an electric field accelerates electrons and holes. The low field case is defined as that in which the applied field is small enough so that the energy gain from the field is small compared to thermal energy and the Maxwell-Boltzmann distribution is not significantly disturbed by the field.

Acceleration of current carriers by the field results in the development of a net drift velocity in the direction of the force. The drift velocity, v_d, developed per unit of electric field intensity, E, is called the "mobility," i.e.,

$$v_d = \mu E. \tag{5}$$

Since each time an electron or hole undergoes a collision its acceleration by the field is interrupted more or less

[20] The small dip seen shortly before the intrinsic line in some of these samples, for example 64, does not indicate a decrease in the number of carriers. What is plotted in Fig. 1 is essentially the reciprocal of the Hall coefficient, which is related to the number of carriers by a proportionality factor which decreases slightly in this range.

effectively, the frequency and nature of the collisions determine the mobility. The collisions which are most important in semiconductors are those with thermal vibrations of the lattice and with ionized donors or acceptors. It is useful to speak of the lattice mobility, μ_L, and the impurity mobility, μ_I, defined as the respective mobilities a charge would develop if one collision or scattering process alone were operative.

For lattice scattering it can be shown that at a given temperature the average distance between collisions is the same for all particles regardless of speed.[21] Faster particles will therefore make more collisions per second, with the result that the mobility will decrease if the average speed of the particles increases. Increasing the temperature decreases the mobility for two reasons: First, the mean speed increases and, second, the average distance between collisions decreases because the lattice vibrations grow more vigorous. The theoretically predicted and experimentally verified result is essentially a $T^{-3/2}$ dependence of the lattice mobility.[22] The mobility measured at room temperature for samples with resistivity greater than a few ohm cm is the lattice mobility since impurity scattering is negligible in this case. Experimental values are listed in Table III. Com-

TABLE III

MOBILITIES IN CM²/VOLT SEC AT 300°K

CARRIER	GERMANIUM	SILICON
Electron	$3,600 \pm 180$[23]	$1,200 \pm 120$[24]
Hole	$1,700 \pm 90$[23]	250 ± 50[24]

[23] J. R. Haynes and W. Shockley, "Mobility and life of injected holes and electrons in germanium," *Phys. Rev.*, vol. 81, pp. 835–843; 1951.
[24] J. R. Haynes and W. C. Westphal, "Drift mobility of electrons in silicon," *Phys. Rev.*, vol. 85, p. 680; 1952.

bining these data and the temperature dependence mentioned above results in the empirical formulas for lattice mobility as a function of temperature which are shown in Table IV.

TABLE IV

LATTICE MOBILITIES IN CM²/VOLT SEC

CARRIER	GERMANIUM	SILICON
Electron	$19 \times 10^6 T^{-3/2}$	$6.2 \times 10^6 T^{-3/2}$
Hole	$8.9 \times 10^6 T^{-3/2}$	$1.3 \times 10^6 T^{-3/2}$

Scattering by ionized donors or acceptors is coulomb scattering, which is less effective as the average speed of the carriers increases and thus as the temperature increases. The impurity mobility calculated theoretically for the case of scattering by ionized impurities is[25]

$$\mu_I = \frac{8\sqrt{2}\kappa^2 (kT)^{3/2}}{\pi^{3/2} N_I e^3 m_{\text{eff}}^{1/2} \ln\left[1 + \left(\dfrac{3\kappa kT}{e^2 N_I^{1/3}}\right)^2\right]}, \quad (6)$$

[21] See, for example, W. Shockley, *op. cit.*
[22] Experimental data of Fig. 5 show small deviation from this.
[25] E. M. Conwell and V. F. Weisskopf, "Theory of impurity scattering in semiconductors," *Phys. Rev.*, vol. 77, pp. 388–390; 1950.

where κ is the dielectric constant, N_I is the total density of ionized impurities, e is the charge on the electron, and m_{eff} the effective mass of the electron or hole. A thorough experimental test of this formula has not as yet been possible. There is evidence over a considerable range of temperatures and impurity densities that it is of the right order of magnitude. It has recently been found that (6) gives correctly the variation of mobility with resistivity observed for electrons in germanium at room temperature, provided the effective mass of an electron is taken as one-quarter the free electron mass.[26] Since there is other evidence for this effective mass for electrons in germanium, this seems to provide a satisfactory verification of the formula at room temperature for this case. For holes the situation may be much more complicated.[27] Approximations made in the derivation of (6) are such that it cannot be expected to be valid at very low temperatures or very high impurity densities.

With the values of the dielectric constants taken as 16 for germanium and 12 for silicon,[28] (6) can be written

$$\mu_I = 8.5 \times 10^{17} \left(\frac{m}{m_{\text{eff}}}\right)^{1/2} \frac{T^{3/2}}{N_I \ln\left(1 + 8.3 \times 10^8 \dfrac{T^2}{N_I^{2/3}}\right)} \text{Ge}$$

$$\quad (7)$$

$$\mu_I = 4.7 \times 10^{17} \left(\frac{m}{m_{\text{eff}}}\right)^{1/2} \frac{T^{3/2}}{N_I \ln\left(1 + 4.5 \times 10^8 \dfrac{T^2}{N_I^{2/3}}\right)} \text{Si.}$$

These mobilities are plotted as a function of temperature for several different impurity concentrations in Fig. 2. For this plot, $(m/m_{\text{eff}})^{1/2}$ has been set equal to 1. This plot can be used to obtain μ_I, or at least an approximate value thereof, at any temperature provided N_I is known. If the density of carriers is known, it is usually a good approximation to take N_I equal to this density.[29] For electrons in germanium a more accurate result will be obtained by multiplying μ_I shown in the graphs by 2, since for these $m_{\text{eff}} \cong m/4$. For convenience, there are also plotted in Fig. 2 the empirical lattice mobilities of Table IV.

To obtain the mobility, μ, from μ_L and μ_I the approximation of taking the reciprocal of the sum of the separate reciprocals is generally used. This frequently provides a very poor approximation, however. An exact calculation can be carried out very simply with the use

[26] P. P. Debye and E. M. Conwell, "Mobility of electrons in germanium," to be published in *Phys. Rev.*
[27] It seems likely that the edge of the valence band is degenerate with consequent complications.
[28] H. B. Briggs, "Optical effects in bulk silicon and germanium," *Phys. Rev.*, vol. 77, p. 287; 1950.
[29] To see that this is not exactly true, consider an n-type sample. Such a sample, apart from a density N_D of donors, will always have some density of acceptors, N_A, where, of course, $N_A < N_D$. These acceptors will trap electrons which would otherwise go into the conduction band. They will therefore be ionized and scatter electrons at all temperatures. If N_{Di} is the density of ionized donors, $N_I = N_D{}^i + N_A$, while $n = N_D{}^i - N_A$.
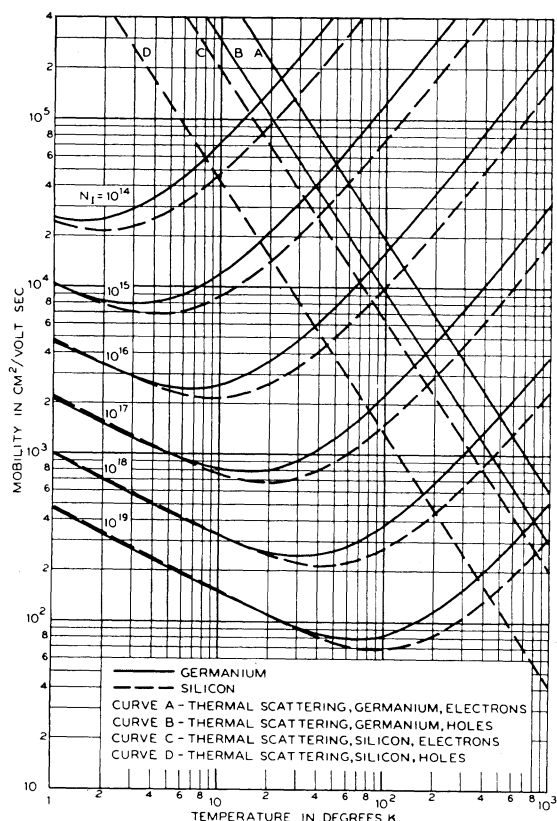
Fig. 2—Impurity and lattice (thermal) scattering versus temperature. The impurity scattering is taken from the theoretical formulas (7) with m/m_{eff} set equal to 1. To use for electrons in germanium, therefore, multiply μ_I by 2. The thermal scattering values are semiempirical, taken from Table IV.

of Fig. 3, which is a graph of the correct relationship between μ/μ_L and μ_L/μ_I. Given the value of μ_L/μ_I, the value of μ/μ_L can be obtained from the graph, and from this the desired value of μ.

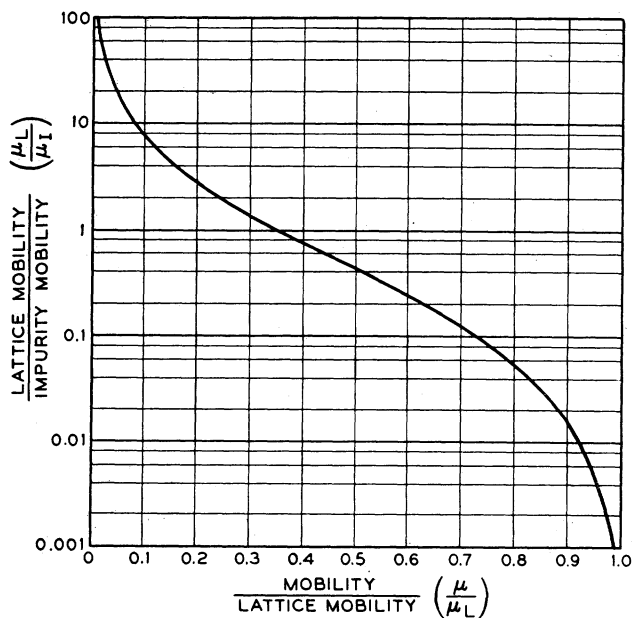Calculation of the mobility for any sample can be

carried out as follows: For a relatively pure sample (resistivity greater than a few ohm cm) the mobility is essentially μ_L, and given by Table IV. For a less pure sample, knowledge of the resistivity enables at least an approximate calculation. Consider an n-type sample for definiteness. Provided that the approximation $N_I = n$ can be used, there is a unique relationship between resistivity and mobility at a given temperature, which can be calculated theoretically. If a value of N_I is assumed, μ_I and then μ can be calculated as previously described. For an n-type sample $1/\rho = ne\mu_n$ (see formula (8)), where e is the charge on the electron. Since $N_I = n$, ρ can then be computed. A set of such calculations for different values of n gives for n-type germanium at room temperature the curve shown in Fig. 4. In these calculations
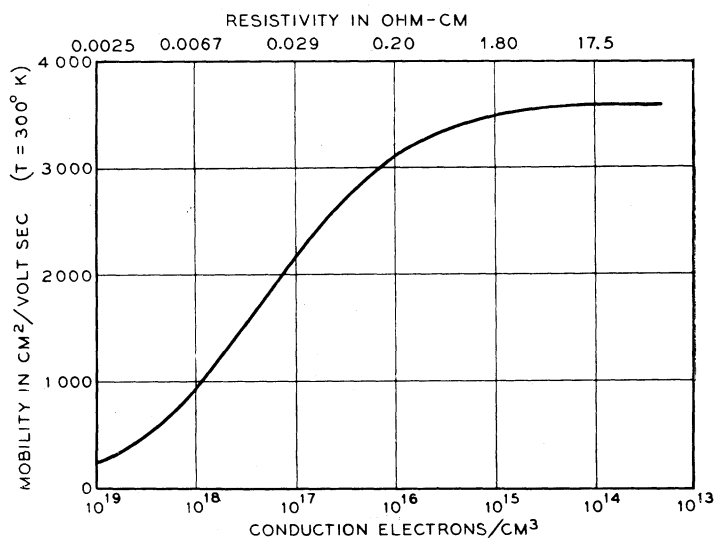
Fig. 4—Mobility versus carrier density and resistivity for n-type germanium at 300°K.

m_{eff} was taken equal to $m/4$. The lower scale shows N_I. This variation of mobility with resistivity has been experimentally verified. Below about 1 ohm cm impurity scattering cuts μ down significantly. This graph will enable immediate determination of the room-temperature mobility and N_I from the room-temperature resistivity. This value of N_I can then be used to compute μ at other temperatures. Similar graphs can be made for p-type germanium and silicon, with less probable accuracy, however, since the effective mass is not known.

We shall consider now, in the light of the previously discussed theory, some typical experimental data on mobility. In Fig. 5 the mobility is plotted on a log-log scale as a function of temperature for the same samples whose concentration data appears in Fig. 1.[30] A line representing a $-3/2$ slope, characteristic of the lattice

Fig. 3—Plot of the theoretical value of μ/μ_L versus μ_L/μ_I.

[30] What is plotted is actually Hall mobility, which is the mobility multiplied by a factor which varies from 1.18 for very pure samples to 1.93 for very impure ones.

mobility, is drawn for comparison. For the purest sample, 55, lattice scattering is dominant to the lowest temperatures at which measurements were made although impurity scattering affects the mobility below
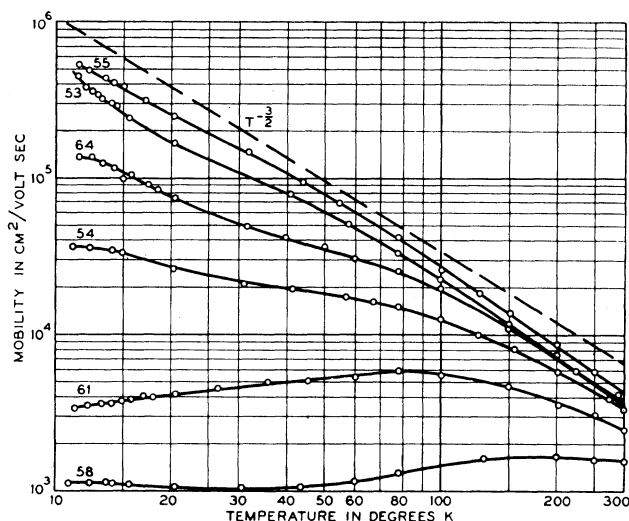

Fig. 5—Mobility versus temperature for the same set of arsenic-doped germanium samples. The data were taken by Debye at Bell Laboratories. The dashed line represents a −3/2 slope characteristic of lattice scattering.

about 70°K. As the impurity content of the samples increases, the mobility is decreased over the entire range and the departure from the $T^{-3/2}$ variation takes place at higher and higher temperatures. In the most impure samples the impurity content is sufficiently high to cause the mobility to start decreasing with temperature, which is characteristic of impurity scattering alone.

High Field Case

In the previously discussed low field case the carriers are able, in collisions with the lattice vibrations, to dissipate the power fed in by the field without their average speed being significantly changed from the thermal value. For this range of fields the mobility is independent of the field, as was discussed previously. When the electric field gets high enough, however, the average electron speed is increased, and the more so the higher the field. An increase of average speed in a sample in which lattice scattering is dominant (such as a fairly pure sample at room temperature) will, as discussed in the preceding section, lead to a decrease in mobility. In such samples, then, it is expected that beyond the range of constant mobility the mobility will decrease with increasing fields. This is found experimentally, as shown in Fig. 6. In this figure there are plotted data for two *n*-type germanium samples, the 298° curve taken for a 3 ohm cm (at low fields) sample, the other two curves for a sample which was 9 ohm cm at room temperature. The impurity concentration was small enough in both these cases so that lattice scattering was more important

than impurity scattering at 77°K as well as 298°K. Beyond the region of constant mobility the mobility decreases as $1/\sqrt{E}$, and at even higher fields, as $1/E$.[31] The latter dependence can be observed at 77°K at higher fields than those obtained in this particular experiment. In general, the departure from constant mobility occurs at lower fields as the temperature decreases. This is expected theoretically because collisions grow less frequent as the temperature goes down, and the rate at which the field supplies energy to the current carriers is higher.

At 20°K in the second sample shown in Fig. 6 impurity scattering was dominant. In this case increase of the average speed of a particle greatly decreases its deflection as it goes by an impurity ion, increasing its mobility. Beyond the region of constant mobility, therefore, the mobility at first rises with field. As a result of this increase in speed the impurity ions become relatively ineffective as scatterers, and collisions with the lattice vibrations become operative in determining the mobility. It is expected, then, that after this rise the $1/E$ variation characteristic of the lattice vibrations takes over, and this is also seen in Fig. 6.
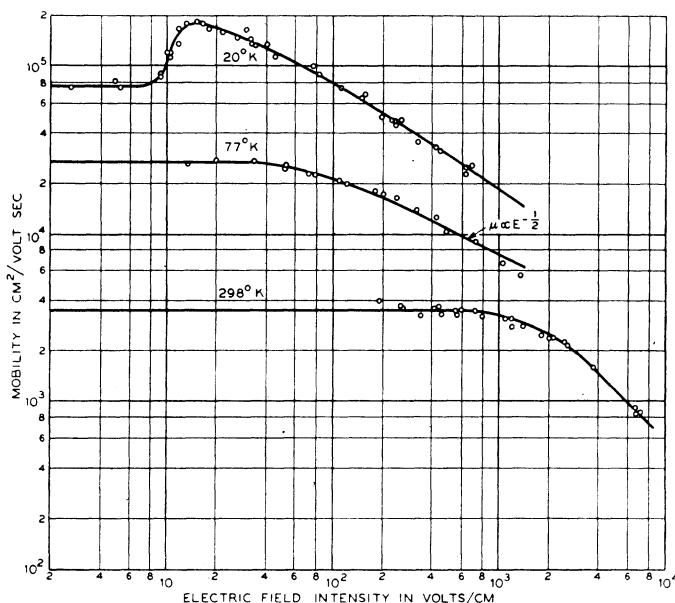

Fig. 6—Mobility versus electric field intensity. The data were taken by Ryder at Bell Laboratories.

These data are typical for fairly pure samples of *n*-type germanium. For less pure samples, the type of variation observed at 20°K would occur at a higher temperature. Approximate values for the field intensity at which departure from constant mobility takes place are listed in Table V. The value for *n*-type silicon is not available.

[31] For theoretical explanation, see W. Shockley, "Hot electrons in germanium and Ohm's law," *Bell Sys. Tech. Jour.*, vol. XXX, pp. 990–1034; October, 1951.

TABLE V

Conductivity Type	Ge	Si
n	900[32]	
p	1,400[33]	7,500[33]

[32] E. J. Ryder and W. Shockley, "Mobilities of electrons in high electric fields,"
Phys. Rev., vol. 81, pp. 139–140; 1951.
[33] E. J. Ryder, to be published in the *Phys. Rev.*

CONDUCTIVITY

The electrical conductivity, σ, and the resistivity, ρ, are related to the concentrations of electrons and holes and their respective mobilities by

$$\sigma = 1/\rho = ne\mu_n + pe\mu_p, \qquad (8)$$

where e is the charge on the electron. The conductivity will therefore be affected by any condition which affects carrier concentrations or mobilities. We shall consider explicitly only its variation with temperature.

For intrinsic material the carrier density and the mobilities can be taken from the empirical formulas given in (4) and Table IV, respectively. This gives

$$\sigma_i = 1/\rho_i = 4.3 \times 10^4 \, e^{-4,350/T} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ Ge,}$$
$$\sigma_i = 1/\rho_i = 3.4 \times 10^4 \, e^{-6,450/T} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ Si.}$$
$$(9)$$

The resistivities of intrinsic material at 300°K computed from these formulas are listed in Table II. Intrinsic conductivity is plotted versus the reciprocal of temperature in Fig. 7 as a dashed line.

Some typical experimental data for the case of extrinsic conductivity are also plotted in Fig. 7. The data shown are for the same set of arsenic-doped germanium samples whose concentration and mobility data are plotted in Figs. 1 and 5, respectively. For sample 58 σ does not vary much with temperature since n and μ do not. It is useful in discussing the other samples to consider various temperature ranges separately. At low temperature, variation of carrier density is the dominant effect. As the temperature rises and donors become ionized, n increases and therefore σ increases. It is interesting to note that in this temperature range samples 53, 64, 54, and 61, which have quite different impurity concentrations, do not differ greatly in conductivity. This can be understood as follows: For these samples impurity scattering is dominant in this range. Their mobility therefore varies approximately inversely with the density of ionized impurities. (See (5). The logarithmic variation with impurity concentration can be neglected.) Since the carrier density is approximately equal to this density, the product of n and μ, and therefore the conductivity, should be approximately the same for all of them.

Over the range of temperatures where the impurities are essentially all ionized and carrier concentration is constant, mobility variation dominates. In this range

lattice scattering is usually dominant, and the conductivity therefore decreases as the temperature increases. At still higher temperatures intrinsic conductivity, described by (9), sets in.
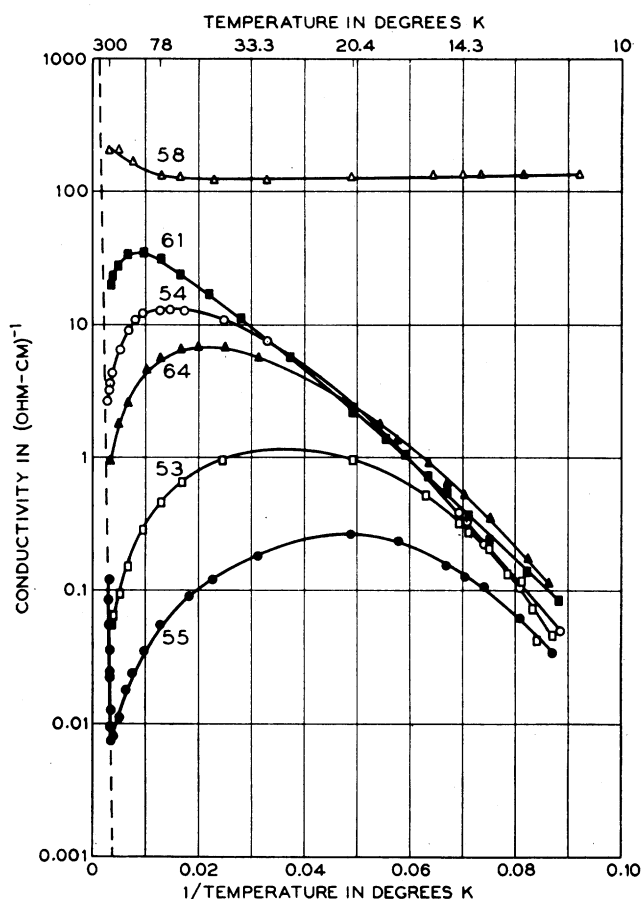

Fig. 7—Conductivity versus absolute temperature for the same set of arsenic-doped germanium samples. The data were taken by Debye at Bell Laboratories. The dashed line represents intrinsic conductivity.

ZENER CURRENT

Application of a strong electric field may enable electrons from the valence band to cross the energy gap which separates them from the conduction band. This involves a process of penetration of a potential barrier very similar to the penetration of the potential barrier at the surface of a metal when a high field is applied to produce cold emission. The resulting current, frequently called "Zener current," is very strongly field dependent. Fields of the strength required to produce a measurable Zener current without undue heating and other undesirable effects may be obtained in the space-charge region of a p-n junction biased in reverse.

A typical reverse current-voltage characteristic for a germanium p-n junction is shown in Fig. 8. For low fields the only carriers available which can cross the junction are the holes in the n-region and the electrons in the p-region. Since these are relatively few in number, this constitutes a small current and one which is practically independent of field since the carriers travel

mainly by diffusion. This accounts for the constant saturation current observed up to about 6 volts in this particular junction. At about 6 volts, however, an additional current starts to flow which increases very sharply with voltage. The field at which the transition takes place and the general behavior of the curve beyond the transition are approximately what is predicted theoretically from a simple picture of the Zener effect. The additional current has therefore been identified as Zener current.[34]
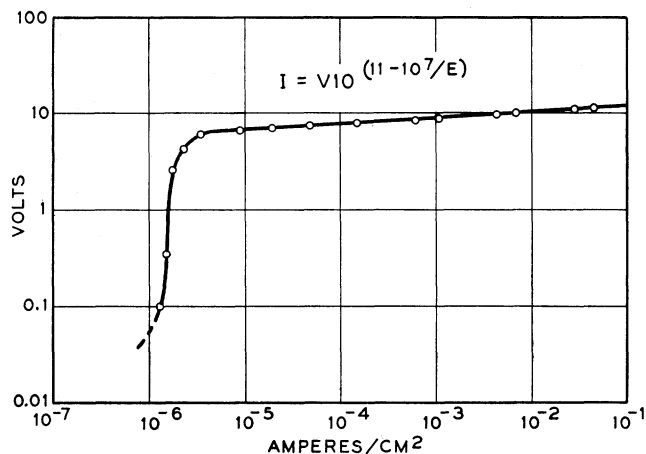

Fig. 8—Current-voltage characteristic for a *p-n* junction biased in reverse. The data were taken from McAfee, Ryder, Shockley, and Sparks.[34] The formula included is derived theoretically from a simple picture of Zener effect, and fits the Zener current for this particular junction quite well.

The field intensity at which the so-called Zener current becomes appreciable compared to the saturation current is called the "critical field." In germanium this has been found to depend on crystallographic orientation. The value obtained when the $|||$ direction of the crystal is perpendicular to the *p-n* interface is 2×10^5 volts/cm. Values found for other orientations in germanium differ by as much as a factor of 2.[35] In silicon there is no evidence for a dependence of the critical field on crystallographic direction. Values have been reported ranging from 2×10^5 volt/cm[36] to 2.5×10^5 volts/cm.[37]

It has also been found that the current-voltage characteristic changes somewhat with temperature. For the

junctions studied the voltage required to produce a particular current in the Zener range increases as the temperature increases at a rate of about 0.1 per cent per degree. This does not necessarily indicate that the critical field varies in this way.

Lifetime

Departure from the thermal equilibrium concentrations of electrons and holes can be obtained by injecting carriers of the minority type, e.g., holes in *n*-type material, say, at a point contact.[38] To maintain electrical neutrality of the specimen an equal number of the majority carrier must be drawn in at the same time. (This process is of importance in many types of transistor action.) The carrier concentrations can also be changed from the thermal equilibrium values by, for example, the creation of hole-electron pairs by light, X-rays, or strong electric fields. When there is an excess of carriers present, the system tends to return to equilibrium by recombination of the excess electrons and holes.

Such recombination has been observed by Haynes and Shockley.[39] They find that a small pulse of holes injected into a filament decays exponentially, so that if N_0 is the original number of injected holes, the number existing after time t is $N_0 e^{-t/\tau_p}$. τ_p, called the lifetime of a hole, is thus the time required for the pulse to decay to $1/e$ of its original size.[40] Analogous results have been obtained for electrons injected into *p*-type material.

Experiments with filaments of varying cross section and surface treatment show that the recombination in general occurs both in the volume and on the surface of the material. The lifetime observed, τ, can be considered to be made up of separate lifetimes for body and surface recombination, τ_v and τ_s, respectively, according to

$$1/\tau = 1/\tau_v + 1/\tau_s. \tag{10}$$

The factors affecting these separate lifetimes will now be considered.

Body lifetime varies very widely from crystal to crystal. It is also a function of temperature for any given crystal. The values to be quoted are for room temperature and small injected carrier density. In both *n*- and *p*-type germanium, values as high as 1,000 μsec have been observed.[41] Typical values for crystals grown

[34] K. B. McAfee, E. J. Ryder, W. Shockley, and M. Sparks, "Observations of Zener current in germanium *p-n* junctions," *Phys. Rev.*, vol. 83, pp. 650–651; 1951. In a number of samples measured since this publication, however, it has been found that the slope of the curve in the Zener region is quite different from the theoretical prediction. The effect observed may thus be more complicated.

[35] K. B. McAfee, private communication, Bell Telephone Laboratories, Inc., Murray Hill, N. J.

[36] K. B. McAfee and G. L. Pearson, abstract E6 in the program of the 1952 Washington meeting of A.P.S. These results were obtained for grown junctions. Also, "The electrical properties of silicon *p-n* junctions grown from the melt," *Phys. Rev.*, vol. 87, p. 190; July, 1952.

[37] G. L. Pearson and B. Sawyer, "Silicon *p-n* junction alloy diodes," Proc. I.R.E., vol. 40, pp. 1348–1352; this issue. These results were obtained for alloy process junctions.

[38] For references and a discussion of the literature see W. Shockley, *op. cit.*, chap. 3

[39] J. R. Haynes and W. Shockley, "Investigation of hole injection in transistor action," *Phys. Rev.*, vol. 75, p. 691; 1949; and vol. 81, p. 835; 1951.

[40] What is actually observed in these experiments and most lifetime-measuring experiments is a quantity called the "diffusion length" rather than the lifetime. Written for holes, the diffusion length, denoted by L_p, is defined by

$$L_p = \sqrt{D_p \tau_p},$$

and is the average distance along any given direction which a hole will diffuse before recombining.

[41] J. R. Haynes, private communication, Bell Telephone Laboratories, Inc., Murray Hill, N. J. However, much higher values have been rumored.

by the pulling method of Teal and Little[42] from originally purified germanium are a few hundred μsec for high-resistivity material (of the order of 30 ohm cm) and 100 μsec for material of about 5 ohm cm. Few data are available for silicon. The values reported are in general lower than those for germanium. As a general trend, the lower the resistivity of the samples the lower the lifetime, but there are frequent exceptions to this.

The great variations from crystal to crystal are due to the fact that body lifetime is quite sensitive to the presence of chemical impurities and imperfections in the lattice. In line with this it has been found that thermal conversion and bombardment both have drastic effects on the lifetime, being able to cut it down from several hundred μsec, for example, to 1 μsec or less. Crystals strained during solidification may have lifetimes as low as a μsec. Doping with column III and V elements in general decreases the lifetime somewhat.

The lifetime for surface recombination, τ_s, depends on the dimensions of the sample as well as on surface properties because the carriers must diffuse to the surface before they can recombine there. It is convenient to separate out the dependence on the surface itself by introducing the surface velocity of recombination, s, defined by

$$s = \frac{\text{number recombining per second per unit surface area}}{\text{excess density over thermal equilibrium value just below surface}}.$$

Values of s have been found ranging from less than 10^2 cm/sec to greater than 10^4 cm/sec, these being correlated with surface treatment. The high value stated is obtained for sandblasted surfaces. If the surface is polished smooth and etched with CP-4 etch to remove worked material, the value of s is decreased to 5×10^2 cm/sec. Chemical treatment of this polished and etched surface can reduce this to about 1×10^2 cm/sec, or increase it to values as high as those obtained for sandblasted surfaces.[43] Values of s less than 10^2 cm/sec have also been reported for etched surfaces.[44]

The relationship among τ_s, s, and the dimensions of the sample has been derived theoretically by Shockley for a rod or filament of rectangular cross section. The results can be expressed simply for the limiting cases of very large s and very small s. For a sample with transverse dimensions $2B \times 2C$, these are

$$\frac{1}{\tau_s} = \frac{\pi^2 D}{4}\left(\frac{1}{B^2} + \frac{1}{C^2}\right) \qquad s \to \infty$$

$$\frac{1}{\tau_s} = s\left(\frac{1}{B} + \frac{1}{C}\right) \qquad s \to 0, \tag{11}$$

where D is the appropriate diffusion constant.[45]

Diffusion of Current Carriers

An electric current can also arise from diffusion of electrons or holes. For specificity we shall speak of holes in n-type material, the modification for electrons in p-type material being obvious. Also, we shall assume there is no externally applied electric field. Consider a situation in which the density of holes varies with position, such as would be the case if holes were being injected at a point. For simplicity we will assume that this variation takes place in one direction only, and has a concentration gradient dp/dx. As a result of thermal agitation there will be a net flow of holes tending to smooth out the inequalities in concentration. In the case in which the injected hole density is much smaller than the electron concentration the holes will disturb the electron distribution very little and will diffuse like a neutral gas. The hole current density, j_p, arising from diffusion is proportional to the concentration gradient of the holes, and is directed oppositely. It can be written for this case of small injected density,

$$i_p = -eD_p\frac{dp}{dx}. \tag{12}$$

This defines D_p, the diffusion coefficient of holes. A diffusion coefficient for electrons, D_n, can be defined similarly.

For small injected hole density the diffusion coefficient is related to the mobility by the Einstein relation,[46]

$$\mu_p = \frac{e}{kT}D_p. \tag{13}$$

A corresponding relation of course exists for electrons. At 300°K for fairly pure germanium samples, the diffusion coefficients calculated from this are

$$D_n = 93 \text{ cm}^2/\text{sec}$$

$$\text{Ge at } 300°\text{K.}$$

$$D_p = 44 \text{ cm}^2/\text{sec}$$

Further numerical values will not be given since the Einstein relation plus knowledge of the mobility makes their calculation simple.

[42] G. K. Teal and J. B. Little, "Growth of germanium single crystals," *Phys. Rev.*, vol. 78, p. 647; 1950.

[43] See J. R. Haynes and W. Shockley, *op. cit.*, for composition of CP-4 etch and details of the chemical treatment.

[44] D. Navon, R. Bray, and H. Y. Fan, abstract E10 in the program of the 1952 Denver meeting of A.P.S. Also, "Lifetime of injected carriers in germanium," *Bull. Amer. Phys. Soc.*, vol. 27, pp. 14–15; June 30, 1952. Also, W. Brattain, private communication, Bell Telephone Laboratories, Inc., Murray Hill, N. J.

[45] For filaments of square cross section, the relationship between τ_s and s for all values of s is given graphically in W. Shockley, *op. cit.*, p. 324.

[46] A. Einstein, "Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flussigkeiten suspendierten Teilchen," *Ann. der Phys.*, vol. 17, pp. 549–560; 1905.

When a large density of holes is injected, the change in the electron distribution due to the holes cannot be neglected. To neutralize the space charge of the holes a correspondingly large density of electrons must accumulate in the neighborhood of the holes and must furthermore move at the same rate. The hole current (or electron current) is, in this case, also proportional to the concentration gradient, but the constant of proportionality is given by eD,[47] where

$$D = \frac{2D_n D_p}{D_n + D_p},\qquad(14)$$

this being the same for electrons and holes. This result applies also to the diffusion of carriers injected into intrinsic material. At room temperature in germanium $D = 59$ cm²/sec.

MAGNETORESISTANCE

Experimental data on the change of resistance in a magnetic field have been obtained by Pearson and Suhl for n- and p-type germanium.[48] They investigated the dependence of the effect on magnetic field strength, temperature, and angle between current and magnetic field. In the case of p-type germanium the fractional change in resistance, $\Delta\rho/\rho$, was considerably larger for the field perpendicular to the current than for the field parallel to the current, while for n-type germanium the reverse was true. The size of the effect was found to increase as the square of the field at low fields and as a lower power of H at high fields. For any given field the effect was found to increase as the temperature was lowered. In the temperature range from 77°K to room temperature, $\Delta\rho/\rho$ was never larger than about 10 per cent for fields up to 1,000 gauss. Very considerable effects were observed, however, for higher fields. At room temperature in n-type material for a field of 100,000 gauss, $\Delta\rho/\rho$ was 1.1 for the field perpendicular to the current, 2.2 for the field parallel to the current. At 77°K $\Delta\rho/\rho$ for the latter case reached 2.0 at a field of 20,000 gauss.

OPTICAL PROPERTIES

We shall consider first the optical absorption of pure material. In Fig. 9, per cent transmission is plotted versus wavelength, λ, in microns (1 micron = 10^{-4} cm) for high resistivity specimens of germanium and silicon. Both absorb strongly in the visible and near infrared, and are relatively transparent over most of the range of longer infrared wavelengths. These qualitative features can be understood readily.

One process by which light can be absorbed in germanium or silicon is through excitation of electrons from the valence band to the conduction band, creating hole-electron pairs. The energy of a quantum required for this transition corresponds to light in the visible and near infrared regions of the spectrum. The lowest energy quantum which would enable an electron to make this transition would have to have energy equal to the energy gap. At the long wavelength limits of the absorption observed in germanium and silicon, the quantum energies agree quite well with the previously given values of the respective energy gaps. It has also been shown experimentally that this process has unit quantum efficiency, i.e., for every quantum absorbed in this range one hole-electron pair is created.[49]
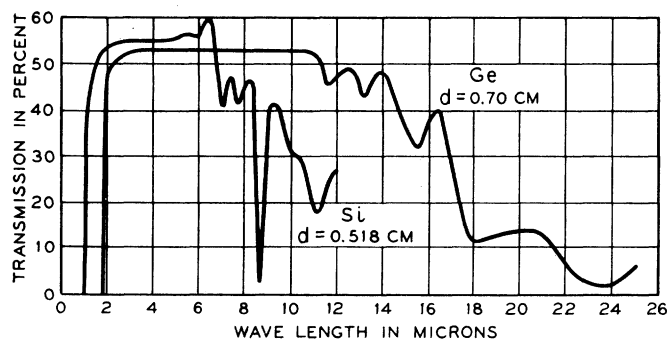

Fig. 9—Per cent transmission versus wavelength for high-resistivity germanium and silicon. The data were taken by Briggs at Bell Laboratories. Thickness of the sample is indicated in each case.

For wavelengths longer than the absorption limit, the energy cannot be absorbed by electrons in the valence band, and the crystals will be relatively transparent. Transmission is only about 50 per cent, however, because of reflection at the surface. The sharp peak at about 9 microns in silicon is probably due to absorption by the lattice.[50] The other absorption observed in the infrared may be due to the free carriers.

Impure samples of germanium and silicon show the same behavior in the visible and near infrared as the pure samples. Beyond the absorption limit, however, they show greater absorption than pure samples. This absorption increases with carrier concentration, and is presumably due to the absorption of the free carriers.

ACKNOWLEDGMENTS

[47] W. van Roosbroeck, "Theory of the flow of electrons and holes in germanium and other semiconductors," *Bell Sys. Tech. Jour.*, vol. 29, pp. 560–607; 1950.
[48] G. L. Pearson and H. Suhl, "Magneto-resistance effect in oriented single crystals of germanium," *Phys. Rev.*, vol. 83, pp. 768–776; 1951.

[49] F. S. Goucher, "Photon yield of electron-hole pairs in germanium," *Phys. Rev.*, vol. 78, p. 816; 1950.
[50] H. B. Briggs, "Infra-red absorption in silicon," *Phys. Rev.*, vol. 77, pp. 727–728; 1950.

THERMAL PROPERTIES

THERMOELECTRIC POWER DEPENDS STRONGLY ON CARRIER DENSITY SO NO VALUES WILL BE GIVEN

TABLE VI

QUANTITY	GERMANIUM		SILICON	
	VALUE	TEMERATURE	VALUE	TEMPERATURE
Linear thermal expansion coefficient	$6.1 \times 10^{-6}/°C$[51] $6.6 \times 10^{-6}/°C$[51]	0–300°C 300–650°C	$4.2 \times 10^{-6}/°C$[57]	10–50°C
Thermal conductivity	0.14 cal/sec cm°C[53] ~0.11 cal/sec cm°C[53]	25°C 100°C	0.20 cal/sec cm°C[54]	20°C
Specific heat	0.074 cal/gm°C[52]	0–100°C	0.181[52]	18.2–99.1°C
Latent heat of fusion	8300 cal/mol[55]		9450 cal/mol[54]	
Melting point	936°C[56]		1420°C[52]	
Boiling point	2700°C[52]		2600°C[52]	

[51] W. L. Bond, private communication, Bell Telephone Laboratories, Inc., Murray Hill, N. J.
[52] "Handbook of Physics and Chemistry," Chem. Rubber Publishing Co., ed. 33.
[53] A. Greico and H. C. Montgomery, "Thermal conductivity of germanium," *Phys. Rev.*, vol. 86, p. 570; 1952.
[54] "Metals Handbook," American Society for Metals; 1948.
[55] See paper by L. Brewer in "Chem. and Met. of Misc. Materials," edited by L. L. Quill, McGraw-Hill Book Co., Inc.; 1950.
[56] E. S. Greiner, private communication, Bell Telephone Laboratories, Inc., Murray Hill, N. J.
[57] M. E. Straumanis and E. J. Aka, "Lattice parameters, coefficients of thermal expansion, and atomic weights of purest silicon and germanium," *Jour. Appl. Phys.* vol. 23, pp. 330–334; 1952.

MECHANICAL PROPERTIES

TABLE VII

QUANTITY	VALUE	
	GERMANIUM	SILICON
Elastic constant C_{11}	12.98×10^{11} dynes/cm² [58]	16.740×10^{11} dynes/cm² [57]
Elastic constant C_{12}	4.88×10^{11} dynes/cm² [58]	6.523×10^{11} dynes/cm² [59]
Elastic constant C_{44}	6.73×10^{11} dynes/cm² [58]	7.957×10^{11} dynes/cm² [59]
Volume compressibility	1.3×10^{-12} cm²/dyne[60]	0.98×10^{-12} cm²/dyne[61]

[58] W. L. Bond, W. P. Mason, H. J. McSkimin, K. M. Olsen, and G. K. Teal, "Elastic constants of germanium single crystals," *Phys. Rev.*, vol. 78, p. 176; 1950.
[59] H. J. McSkimin, W. L. Bond, E. Buehler, and G. K. Teal, "Measurement of the elastic constants of silicon single crystals and their thermal coefficients," *Phys. Rev.*, vol. 83, p. 1080; 1951.
[60] Calculated from the elastic constants.
[61] P. W. Bridgeman, "Linear compressions to 30,000 kg/cm² including relatively incompressible substances," *Proc. Amer. Acad. Arts and Sci.*, vol. 77, no. 6, pp. 187–234; 1949.

MISCELLANEOUS

TABLE VIII

QUANTITY	VALUE	
	GERMANIUM	SILICON
Atomic number	32	14
Atomic weight	72.60[57]	28.08[57]
Lattice constant	5.657×10^{-8} cm[57]	5.431×10^{-8} cm[57]
Density	5.323 gm/cm³ [57]	2.328 gm/cm³ [57]
Dielectric constant	16[28]	12[28]
Magnetic susceptibility	-0.12×10^{-6} cgs[52]	-0.13×10^{-6} cgs[52]
Debye temperature	290°K	